

ON THE LIQUID PHASE CHEMISTRY OF THE LIGHT HYDROGEN ISOTOPE MUONIUM

Inaugural-Dissertation

zur Erlangung der philosophischen Doktorwürde

vorgelegt der

Philosophischen Fakultät II

der

Universität Zürich

von

EMIL RODUNER

aus Sennwald SG

Begutachtet von Herrn Prof. Dr. Hanns Fischer

1980

Zürich 1979

Zentralstelle der Studentenschaft

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OF THE LIGHT HYDROGEN
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ON THE LIQUID PHASE CHEMISTRY
OF THE LIGHT HYDROGEN
ISOTOPE ALUMINUM

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1. INTRODUCTION

Muonium (Mu) is the exotic atom consisting of a positive muon and an electron. The muon is an elementary particle and is classified as a lepton, together with the electron and the neutrino. μ^+ , the antiparticle of μ^- , is not only of interest to particle physicists, but has found wide applicability in solid state physics and in chemistry. Its analogy with protons (table 1.1) led to its use as a proton substitute in the study of magnetic interactions in matter. The experimental technique has been dubbed μ SR (muon spin rotation) and rests on the following principles: Spin polarized positive muons are stopped in the target to be investigated. Subsequently, interaction of the μ^+ magnetic moment with local magnetic fields of the environment and/or an externally applied magnetic field causes evolution of the spin polarization in time and space. Decay positrons ($\tau_\mu = 2.2\mu\text{s}$) are emitted preferentially along the instantaneous muon spin directions. Thus, counting decay positrons in a given direction as a function of the time spent in the target by the corresponding muons gives information about the time evolution of μ^+ spin polarization in that direction. Histograms obtained in this way are radioactive decay curves modulated with the muon precession frequencies. Fourier analysis or direct fitting reveals these frequencies, their amplitudes, phases and relaxation rates.

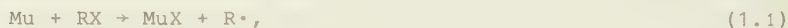
The chemical significance of μ^+ is based on its role as the nucleus of the Mu atom. Although the muon rest mass is only $1/9$ that of the proton, the Mu atomic Bohr radius and ionization potential are within 0.5% of those of H.

Table 1.1: Muon and muonium properties

μ^+	mass	0.11261 mass of proton
	spin	$\frac{1}{2}$
	magnetic moment	3.18334 proton magnetic moment
	lifetime	2.1971 μ s
Mu	Bohr radius, a_0	$0.5317 \text{ \AA} = 1.0043 a_0(\text{H})$
	ionization potential, I	$13.539 \text{ eV} = 0.9957 I(\text{H})$

Thus, from a chemical point of view, Mu is a light isotope of hydrogen and may be expected to undergo analogous reactions [1]:

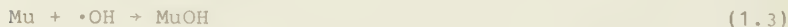
- abstraction (of H, Br):



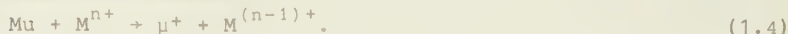
- addition, e.g.



- radical combination, e.g.



- electron transfer



Three different classes of muonic compounds are distinguishable by means of their characteristic muon precession frequencies which are a function of the applied magnetic field transverse to the μ^+ spin direction:

1. Muons substituted in diamagnetic molecules (e.g. MuOH) precess at their nuclear Larmor frequency, $\nu_\mu = 13.55 \text{ kHz/G}$. The resolution of a conventional μ SR apparatus is such that the small chemical shifts typical in proton NMR are not discernable.

2. Mu is a two-spin- $\frac{1}{2}$ system, so its precession signal is more complicated than that of a single muon. In the absence of an external field, the spins combine to give a singlet and a triplet. The variation of the four energy levels as a function of magnetic field strength is given by the Breit-Rabi diagram (fig.1.1).

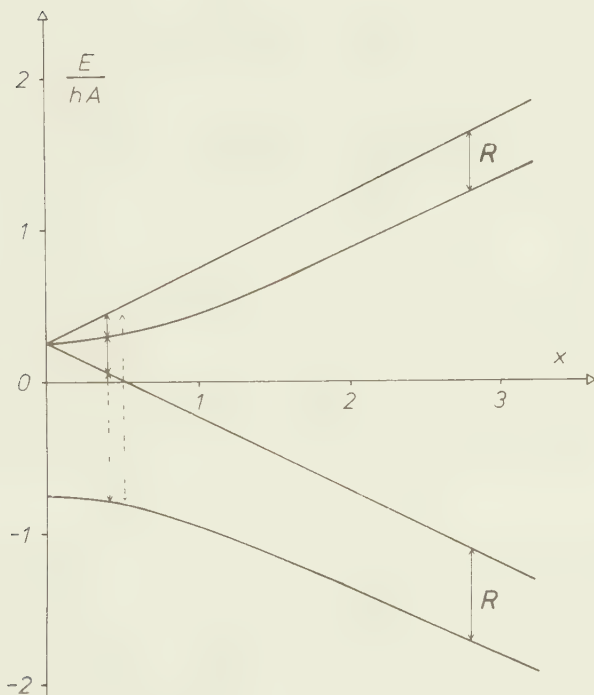


Fig.1.1: Breit-Rabi diagram for two-spin- $\frac{1}{2}$ system [2].

The dimensionless field parameter x is given by

$$x = \frac{\nu_e + \nu_\mu}{A} , \quad (1.5)$$

where ν_e and ν_μ are the electron and muon Larmor frequencies ($\nu_e = 2.80247$ MHz/G) and A is the isotropic

hyperfine coupling constant (= 4463 MHz for Mu).

In general, Mu is not prepared in one of these eigenstates. Therefore the system will oscillate between such states. In μ SR experiments we observe the evolution of muon spin polarization during these oscillations. For fields transverse to the muon polarization, four transitions are allowed, giving rise to four characteristic μ SR precession frequencies. Two of these, depicted by dotted lines in fig.1.1 are too high to be resolved by conventional μ SR apparatus. The remaining two, denoted by full lines, become degenerate for fields ≤ 20 G. This is the so-called "muonium frequency" (1.394 MHz/G) which is used to characterize Mu.

3. Muonium substituted radicals as obtained by reaction (1.2) are usually multi-spin systems. In high magnetic fields, however, the spins are decoupled. Here, as will be shown in Chapter 4, we neglect additional magnetic nuclei and treat the system as Mu with a reduced hyperfine interaction. The observable transitions are designated R in fig.1.1.

At the start of this work the diamagnetic signal only had been found in the majority of substances investigated. Mu had been detected in certain rare gases [3,4], in quartz, solid CO₂ and ice [5,6] as well as in the semiconductors silicon and germanium [6,7], and more recently in liquid water [8]. For reasons unknown at that time muonic radicals had not been observed directly despite much effort. Nevertheless, there was some indication of the occurrence of such species [9]. The rate constant for the bimolecular reaction of Mu with Br₂ in the gas phase had been determined directly by measuring the damping on the muonium precession as a function of substrate

concentration [10]. Reactions of Mu in the liquid phase had been studied by an indirect method [9]. Deduced rate constants are model dependent and appear sometimes unrealistically high.

The scope of this work is twofold:

- To measure directly rate constants for bimolecular reactions of Mu in aqueous solution, compare them to analogous values for the reaction of H and interpret the expected isotope effects on the basis of reaction rate theories.
- To give the theoretical foundations for a first observation and a basic understanding of muonic radicals.

2. EXPERIMENTAL AND ANALYSIS

2.1. The μ SR Technique

All experiments were carried out in the μ E1 and μ E2 areas of the Swiss Institut for Nuclear Research (SIN) in Villigen. Polarized positive muons are produced in the following way:

Protons are accelerated in an isochronous injector cyclotron to an energy of 72 MeV and then fed into a second cyclotron where they are accelerated to 590 MeV and subsequently focussed on a suitable target (usually Be). Pions produced in the resultant nuclear interactions then decay via the weak interaction (with a mean lifetime of 26 ns), according to the process

$$\pi^+ \rightarrow \mu^+ + \nu_\mu. \quad (2.1)$$

Since the pion has zero spin and the spin- $1/2$ neutrino (ν_μ) has negative helicity (spin antiparallel to its momentum), the conservation of angular momentum forces the spin- $1/2$ muon to also be 100% polarized with the spin antiparallel to its momentum in the rest frame of the π^+ . At SIN the pions decay in-flight in an 8m long superconducting solenoid with a longitudinal magnetic field of 50 kG which collects all muons. Forward and backward decay muons (in the π^+ rest frame) have opposite polarization in the laboratory frame. Under normal operating conditions "backward" muons with a momentum of 115 MeV/c and a polarization of $\sim 80\%$ are selected from the decaying pions ($p_\pi = 220$ MeV/c). The muons are stopped in the sample where they decay with a lifetime of 2.2 μ s according to

$$\mu^+ \rightarrow e^+ + \bar{\nu}_\mu + \nu_e. \quad (2.2)$$

Spin and momentum must again be conserved in this three-particle decay. This causes the angular distribution of

positrons to be anisotropic. The e^+ emission probability is proportional to $1+a\cdot\cos\theta$, where θ is the angle between the muon spin and positron momentum direction. The asymmetry a is a function of the energy of the emitted e^+ with an average value of $\frac{1}{3}$, and a maximum value of 1 (for positrons of maximum energy, 52 MeV). As a result the variation of positron detection reflects the evolution of muon spin polarization.

All experiments reported here were performed in a magnetic field transverse to the μ^+ spin direction. The experimental set-up is shown schematically in fig.2.1. The muon beam is usually reduced to a diameter of 15 mm by passage through a lead collimator. Muons are slowed down in polyethylene (in the collimator hole) and in a water degrader which is continuously adjustable to maximize the number of stopped muons in the sample. Charged particles are observed by means of plastic scintillation counters. The resulting electrical pulses are analysed using coincidence units. To stop in the sample a muon must pass through counters a and b but not c. Thus the muon stop signature is $a\cdot b\cdot\bar{c}$. Correspondingly, $\bar{b}\cdot c\cdot d$ represents e^+ emission in the forward (muon beam) direction. The two signatures form the start and stop signals for a lifetime counting apparatus consisting of a time-to-amplitude converter, a fast analog-digital converter and a multichannel memory. Associated logic units serve to reject imperfect events. Only unequivocal single μ^+ stop/ correlated e^+ emission events are retained.

In the absence of a magnetic field (or for unpolarized muons) the histogram accumulated in the multichannel analyzer would depict a single exponential with decay time τ , the muon lifetime. Precession of the muon spin in a magnetic field results in oscillation of the e^+ detection pro-

bability in the positron "telescope", and gives rise to the wiggles shown in fig.2.2.

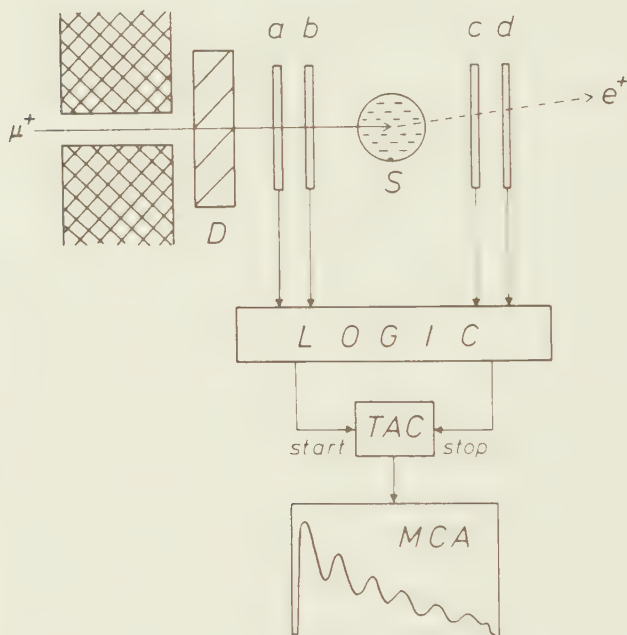


Fig.2.1: Schematic representation of a μ SR experimental assembly [2]. Individual muons pass through the collimator, slow down in the degrader (D) and stop in the sample (S), where they decay. Scintillator counters (a,b,c and d) detect the passage of the muon and also the decay positron if it is emitted in a suitable direction. The muon lifetime is registered by the time-to-amplitude converter (TAC) and a time histogram is accumulated in the multichannel analyzer (MCA).

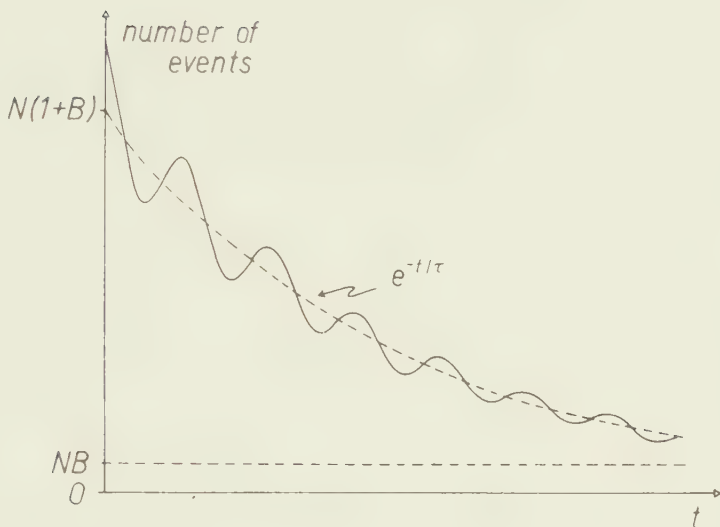


Fig.2.2: Schematic representation of a μ SR histogram [2]. The ordinate denotes the number of muons which decay to emit their positrons in a particular direction. t is the individual muon lifetime.

The general form of the histogram is

$$H(t) = N\{B + e^{-t/\tau} [1 + F(t)]\}, \quad (2.3)$$

where N is the normalization factor, roughly the number of counts in the first channel, and B is a constant background (usually $< 1\%$). $F(t)$ reflects the time dependence of the muon polarization, and thus contains the information of interest. In general it consists of a sum of contributions $F_i(t)$ of the form

$$F_i(t) = A_i e^{-\lambda_i t} \cos(\omega_i t + \phi_i), \quad (2.4)$$

describing a muon precession signal on a characteristic frequency ω_i with a damping λ_i and an initial phase ϕ_i . The amplitude (asymmetry) A_i includes the initial muon polarization in the beam, the asymmetry coefficient a describing the anisotropy of the positron distribution in the muon decay, and the solid angle of the telescope. Thus A_i for a given sample changes with varying experimental conditions. More useful is the fraction of muon polarization

$$P_i = P_S \cdot A_i / A_S, \quad (2.5)$$

where A_S is the asymmetry of a standard sample, measured under the same experimental conditions. Here, CCl_4 served as this standard ($P_S = 1$), but often water was used as a secondary standard ($P_S = 0.622 \pm 0.006$ on the muon Larmor frequency [11]). For the present set-up $A_S(\text{CCl}_4)$ is typically 0.2.

Two histograms are collected simultaneously. The second telescope (not shown in fig.2.1) counts positrons emitted in a direction perpendicular to the muon beam. Each histogram is divided into 4096 bins with a width of 0.4 - 1.7 ns, depending on the frequency or resolution to be obtained. Frequencies up to ≈ 600 MHz are observed with the present apparatus. The resolution is essentially limited by the natural line width $\delta\nu = (\tau \cdot \pi)^{-1} = 0.14$ MHz [12] due to the short lifetime of the muon. 1 - 20 million events are collected in the two histograms at a rate of typically 2500 good events per second ($\approx 10\%$ of the stopped μ^+).

The magnetic field is produced by a pair of coils which are driven by a 6V battery in order to produce a stable field of ~ 4 G for muonium studies. Higher fields (up to 6 kG) are obtained with suitable dc power supplies.

2.2. Sample Preparation and Handling

Substances of the highest commercially available grade (usually Fluka or Merck) and deionized water were used. Liquids and solutions were degassed on a vacuum line via three freeze-pump-thaw cycles, and then sealed, usually in standard thin-walled spherical glass bulbs of 25 mm diameter. For temperatures below ambient the sample was placed in a styrofoam cup and cooled by passage of cold, temperature regulated nitrogen gas. The temperature was measured with a copper-constantan thermocouple in contact with the sample, and was estimated to be accurate to 2 K.

2.3. Data Analysis

During most of the work μ SR histograms were accumulated in a PDP 11/40 computer. This allowed a preliminary analysis by on-line Fourier transformation after correcting the histograms for the exponential decay. Data were recorded on magnetic tape. Final analysis was off-line at the CDC 6400/6500 installation of the Eidgenössische Technische Hochschule, Zürich. Fourier analysis served to check for the presence (or absence) of a signal and to determine its frequency. This was sufficient for most radical runs in this work. Relaxation rates, important for Mu kinetics, were obtained by fitting a theoretical expression (equation 2.3) to the data. A multi-parameter function minimization programme [13] was used to minimize the value of χ^2 given by

$$\chi^2 = \sum [y_i(\text{calc.}) - y_i(\text{exp.})]^2 / y_i(\text{calc.}), \quad (2.6)$$

where $y_i(\text{exp.})$ is the experimental count in bin i and $y_i(\text{calc.})$ is the value calculated from the theoretical expression using the current values of the fit parameters.

The quantity

$$R = \chi^2 / (n-m) \quad (2.7)$$

was taken as a measure for the quality of the fit. n is the number of data points and m the number of parameters in the fit. For a good fit R is close to unity, and most values are found between 0.8 and 1.2. For systematic deviations R increases and unfortunately, it becomes dependent on the magnitude of y_i [14].

Usually bins in the original histogram were grouped together before analysis. It was found that this does not affect the results in a run of usual counting statistics if a minimum of 8 bins per periode of the highest frequency were present.

Fig.2.3 shows a μ SR histogram and the diamagnetic signal $F_D(t)$ for water at 200 G. The solid line represents the best fit of equation (2.3) to the experimental points. The six fit parameters were N , B , A_D , λ_D , ω_D , ϕ_D . For liquid samples λ_D did never deviate significantly from zero, and thus it was often fixed at this value.

Fig.2.4 displays $F(t)$ observed in water at 4.6 G. The wiggles represent the Mu signal F_M , whereas F_D appears as an almost constant displacement from 0. The two signals are almost uncorrelated in the fit, which allows us to treat them separately. F_D has the higher amplitude and was fitted first. Since only a small fraction of a period is observed the signal is not accurately determined, and its parameters are highly correlated. Thus, to save computing time, B and λ_D were fixed at zero and $\omega_D/2\pi$ at 0.06 MHz. To determine F_M its parameters A_M , λ_M , ω_M and ϕ_M were released, and A_D and ϕ_D fixed at their fitted values. The procedure outlined here was standard for the analysis of histograms

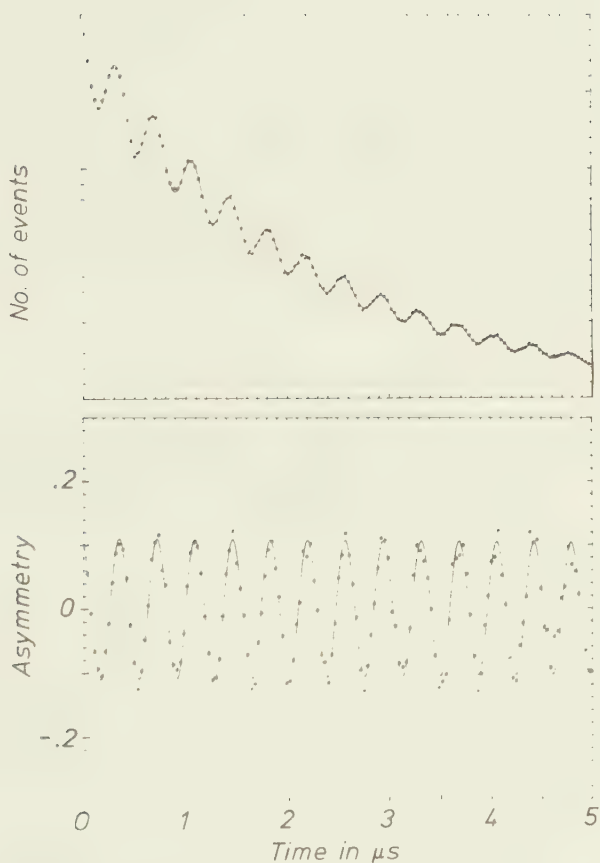


Fig. 2.3: μ SR histogram (upper) and diamagnetic signal (lower) from water in a transverse magnetic field of 200 G [2]. The precession signal, $F_p(t)$ is obtained from the histogram by subtraction of the background and removal of the exponential muon decay.

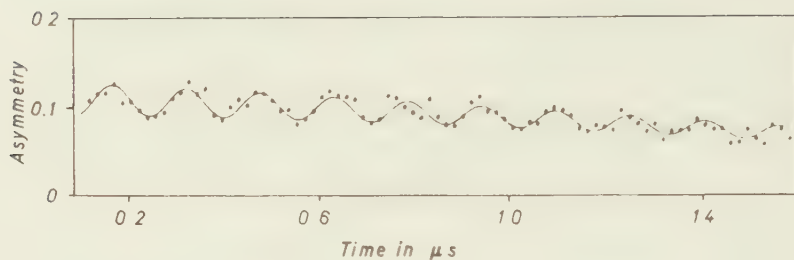


Fig.2.4: Precession signal obtained with water in a transverse magnetic field of 4.6 G. The wiggles represent the muonium signal $F_M(t)$, whereas the offset from zero stems from the diamagnetic signal $F_D(t)$.

for Mu kinetics. The error in the parameter of main interest, λ_M , was determined using a standard routine of the programme [13]. Thereby, λ_M was offset from its best fit value, and χ^2 (eq.2.6) calculated for reoptimized values for the remaining free parameters. Error bars correspond to an increase of unity in χ^2 .

Values of λ_M plotted against concentration of the reacting substrate must lie on a straight line with the rate constant k_M as slope and the relaxation rate in the pure solvent, λ_0 , as intercept (see Section 3.2). Accordingly, values for k_M were obtained from weighted least squares fits of a straight line to at least eight values of λ_M for several different substrate concentrations. The square of the inverse relative error in λ_M was taken as the weight.

Errors quoted for the rate constants correspond to one standard deviation in the slope.

Histograms containing information about a radical are more difficult to fit. The two radical frequencies are often of the same order of magnitude as the muon Larmor frequency, and consequently three signals of the type (2.4) have to be fitted simultaneously. A good fit ($R = 0.9$) was obtained for a histogram taken with benzene at 1 kG (fig. 2.5). No information from such fits was used in this work.

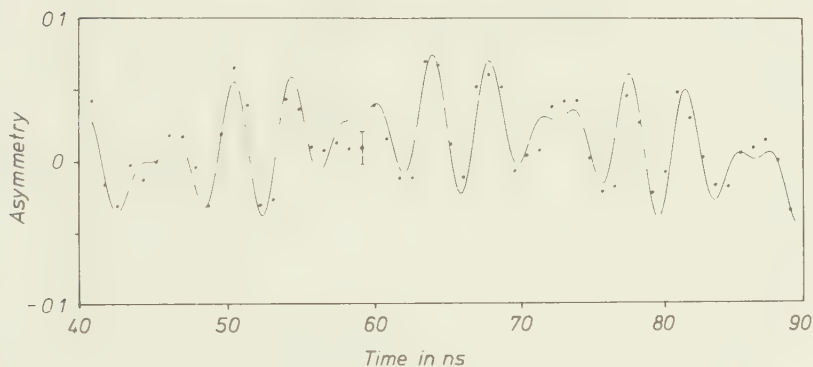


Fig.2.5: Precession signal obtained with benzene in a transverse magnetic field of 1 kG. The two radical frequencies lead to the apparent beats. Only half a period of the diamagnetic signal $F_D(t)$ is shown. The error bar corresponds to $\pm N^{1/2}$, the statistical fluctuation of counts in a bin.

3. MUONIUM KINETICS

Investigating rates of reactions and trying to understand rate processes at the molecular level have formed an important part of chemistry in this century. Since all interatomic and intermolecular forces depend essentially upon nuclear charges and electronic structures and only to a very minor extent upon nuclear masses, two isotopes of the same element, or compounds derived from them, were originally believed to have identical chemical and physical properties [15]. Soon after the discovery of Deuterium in 1931 it was found that the replacement of H by D often has a major effect on the rate of reactions in which bonds involving these isotopes are formed or broken. The isotopic dependence of reaction rates is called a kinetic isotope effect. Comparison of experimental and predicted kinetic isotope effects has been used frequently to test reaction rate theories. The inclusion of Mu in the series of hydrogen isotopes (the relative masses of T, D, H, Mu are 3:2:1:0.11) greatly increases the scope of such studies. The expected large isotope effects may be very discriminative for different theoretical investigations. In particular the lightness of Mu should be sensitive for testing the influence of tunneling in chemical reactions.

In most existing investigations of primary kinetic isotope effects in liquids the isotope is the atom to be transferred (abstracted). In this work the isotope is the attacking species. The major difference is that in the former but not in the latter case the reactants differ in their zero point vibrational energy. In the following chapter the basis for the theoretical interpretation of muonium rate constants is briefly summarised.

3.1. Theoretical Approaches

3.1.1. Activated Complex Theory

Activated complex theory (transition state theory, or absolute rate theory) of chemical reactions has proved to be very useful in interpreting rate data on a wide variety of chemical reactions [16], including reactions in solution. Some major assumptions are concealed in this theory [16, 17]:

- The potential energy of the reacting system, described by N coordinates, changes in a continuous way from that of the reactants to that of the products. An (N-1)-dimensional hypersurface can be defined as having the property that a system that has crossed it has thereby reacted. All the configurations belonging to this hypersurface are called activated complex.
- There is an equilibrium between reactants and systems crossing this hypersurface in the forward direction. It is treated by the standard methods of statistical thermodynamics.
- When quantum mechanical effects are important in the rate of crossing the hypersurface, one usually assumes that the motion across the surface can be treated as a rectilinear motion and that the relevant quantum mechanics for rectilinear tunneling can be applied.

Based on these assumptions the following expression for the rate constant of a reaction is deduced:

$$k_x = \frac{kT}{h} \cdot \frac{Q^\ddagger}{Q} \cdot \Gamma \cdot \exp(-E_0^\ddagger/kT). \quad (3.1)$$

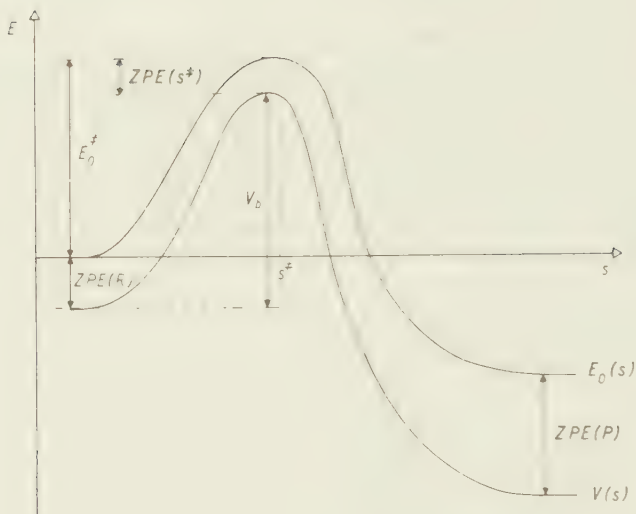


Fig.3.1: A section through the energy hypersurface along the reaction path s between reactants R and products P.

$V(s)$: potential energy

ZPE : zero point energy of the vibrational degrees of freedom excepting the one corresponding to motion along s .

$E_0(s) = V(s) + ZPE(s)$: ground state vibrational adiabatic energy

V_b : classical barrier height

$E_0^\ddagger$: quantum mechanical barrier height

Here, k and h are Boltzmann's and Planck's constant respectively. Q is the partition function of the reactants at a given temperature and volume, and $Q^\ddagger$ is the partition function for all degrees of freedom of the activated complex apart from motion along the reaction coordinate s .

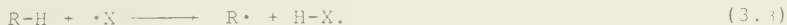
Partition functions are evaluated relative to the lowest accessible energy of the species. Consequently zero point vibrational and potential energies are contained in E_0^+ (see also fig.3.1). Γ is the tunneling factor and is defined as the ratio between the quantum mechanical and the classical rate constant:

$$\Gamma = \frac{\exp(E_0^+/kT)}{kT} \int_0^\infty \kappa(E) \exp(-E/kT) dE, \quad (3.2)$$

where $\kappa(E)$ is the transmission probability of the system per collision with the barrier. In the absence of tunneling we have $\kappa=0$ for $0 \leq E \leq E_0^+$ and $\kappa=1$ for $E_0^+ \leq E \leq \infty$ and therefore $\Gamma=1$.

3.1.2. The Bond-Energy Bond-Order Approach

In general the energy hypersurface and other properties of the reacting system are known from spectroscopic and thermodynamical data only near configurations corresponding to reactants and products. While ab-initio surfaces have been calculated only for a few simple reactions, semi-empirical (in particular LEPS [18]) surfaces have been used more often. A much simpler empirical approach is the BEBO (bond-energy bond-order) method [19, 20] which yields surprisingly reasonable results for activation energies of reactions [16]. It is applied here for abstraction of hydrogen by attacking X ($\equiv$ H, Mu)



An important approximation which is made in the majority of calculations for simple atom-diatom reactions is the principle of collinearity, i.e. the assumption that all nuclei of the triatomic complex lie on a straight line. Calculations of the energy hypersurfaces for the reactions $H+H_2$ [21] and $H+F_2$ [22] show that the collinear configuration indeed corresponds to an energy minimum. It is not

unreasonable to assume that the reaction probability is highest for reaction along the path of minimum energy. It is only the energy along this path, i.e. not the two dimensional energy surface, which is predicted by the BEBO model. The method relies on the following basic assumptions [19]:

- For the path of lowest energy between reactants and products the sum of the bond orders (of the R-H bond being broken and the H-X bond being formed) is constant and equals unity. The term "bond order" is understood according to Pauling's definition [23]

$$R_s - R = C \ln n, \quad (3.4)$$

where R is the bond length at bond order n , R_s is the length of the single bond ($n = 1$) and C is a constant, found to be 0.26.

- The energy of a fractional bond of order n is given by the bond-energy bond-order (BEBO) relationship

$$D = D_s \cdot n^p, \quad (3.5)$$

p being an empirical parameter close to unity but varies slightly depending on the actual bond.

- The potential energy of the triatomic complex (relative to the energy of the reactants) as a function of the progress variable n can be written as the sum of two terms describing the energies of the two fractional bonds (3.5) and a term V_{Tr} describing the triplet repulsion between the two end atoms:

$$V(n) - D_{1s} = -D_{1s} \cdot n^p - D_{2s} \cdot (1-n)^q + V_{Tr}(n). \quad (3.6)$$

$D_{1s}(D_{2s})$ and $p(q)$ are the bond energy and the BEBO parameter for the bond being broken (formed). V_{Tr} is obtained from an anti-Morse function [19] with parameters determined from spectroscopic data.

$V(n)$ ($1 \leq n \leq \infty$) is equivalent to $V(s)$ ($+\infty \geq s \geq -\infty$, $s=0$ chosen at V_{Max}) in fig. 3.1 and is transformed using the relation

$$ds^2 = dR_1^2 + dR_2^2 \quad (3.7)$$

which becomes with (3.4)

$$ds^2 = (0.26)^2 [1/n^2 + 1/(1-n)^2] dn^2. \quad (3.8)$$

In addition to $V(s)$ the BEBO model predicts the properties of the activated complex. Using an empirical relationship between bond order and force constant, Johnston and Parr [19] arrive at expressions for the force constants in Wilson's F-matrix [24]. This allows one to determine the vibrational frequencies for the symmetric stretching and the bending modes (and the associated zero point energies) as well as the imaginary frequency for the asymmetric stretching mode which corresponds to the reaction coordinate.

3.1.3. Tunneling Corrections

The importance of tunneling effects in particular for reactions involving H-atom transfer below ambient temperature has been recognized in recent years [25]. An exact calculation of the tunnel correction is impossible without knowing the effective energy surface for the reaction. In view of the complications the one-dimensional barrier along the minimum energy path is commonly used to represent this correction. Good agreement between exact and one-dimensional results has been demonstrated for the reactions $Mu(H,D,T) + F_2(Cl_2)$ [26].

Analytical expressions for the transmission coefficient κ (3.2) can be given for particular shapes of barriers such as rectangular [27], inverted parabolas [27a] and Eckart barriers [28]. For any one-dimensional barrier κ can be computed by the simple numerical procedure as given by Le Roy, Quickert and Le Roy [29].

κ depends on the energy and the mass of the particle impinging on the barrier. Now, in a simple R_1-R_2 space for the potential surface of our collinear reaction m depends on the two coordinates. It is therefore convenient to use a skewed, mass weighted coordinate system [16, 17]. Here motion is described by a constant effective mass m^* .

The minimum energy path in any coordinate system is curved, but curvilinear effects are usually neglected [16] (see [30] for a discussion of these effects).

If we assume vibrational adiabaticity, i.e. conservation of vibrational quantum numbers, the effective one-dimensional barrier $E_n(s)$ is a continuous curve between the n 'th vibrational level in reactants, activated complex and products. In collinear reactions $E_n(s)$ is taken as the sum of the potential energy $V(s)$ and the vibrational energy of the R-H stretching mode, which evolves smoothly through the symmetric stretching mode of the activated complex to the H-X stretching mode in the product. The energy of the bending modes of the triatomic complex is included only for non-linear collisions [16]. The asymmetric stretching mode corresponds to the reaction coordinate and does not contribute to $E(s)$. The principle of adiabaticity implies the assumption of separability of the vibrational modes.

3.2. Experimental Results

The direct way to determine rate constants for chemical reactions of Mu with a substrate in a concentration [S] is to measure the damping rate λ_M (2.4) of the precession signal on the muonium frequency. The fraction of Mu atoms that has not reacted at time t contributes to the signal. The probability W(t) that Mu has not reacted or relaxed decreases in time according to

$$\frac{dW}{dt} = -W(t) \{ k_M [S] + \lambda_o \} . \quad (3.9)$$

k_M is the rate constant for the bimolecular reaction of type 1.1, 1.2 or 1.4 and λ_o is the damping rate in the pure solvent.

In the course of an experiment 10^8 - 10^9 muons are stopped in the target, and there is a negligible effect on [S]. Thus, integration of (3.9) yields the pseudo-first order rate law

$$W(t) = W(o) e^{-\lambda_M t} \quad (3.10)$$

with

$$\lambda_M = \lambda_o + k_M [S] . \quad (3.11)$$

The damping of the Mu signal increases with increasing substrate concentration, and k_M is obtained as the slope in a plot of λ_M vs. [S]. This behaviour is illustrated in figs. 3.2 - 3.4.

Rate constants have been determined for various solutes in aqueous solution at ambient temperature. They are listed for different classes of reactions in table 3.1 and compared to the corresponding H-atom data. The mode of reaction of H-atoms is usually known and is assumed to be the same for Mu. H reacts with alcohols by abstraction of an aliphatic H-atom, preferentially the one which is most weakly bound [1, 36].

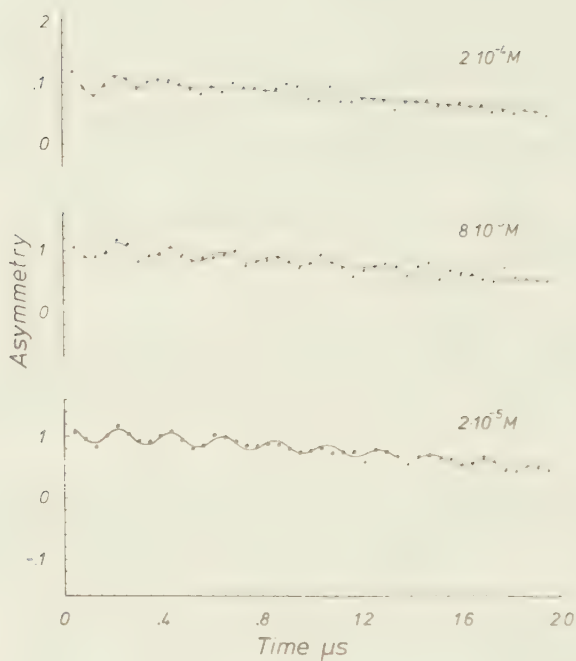


Fig.3.2: Damping of the muonium signal due to chemical reaction with fumaric acid of different concentrations.

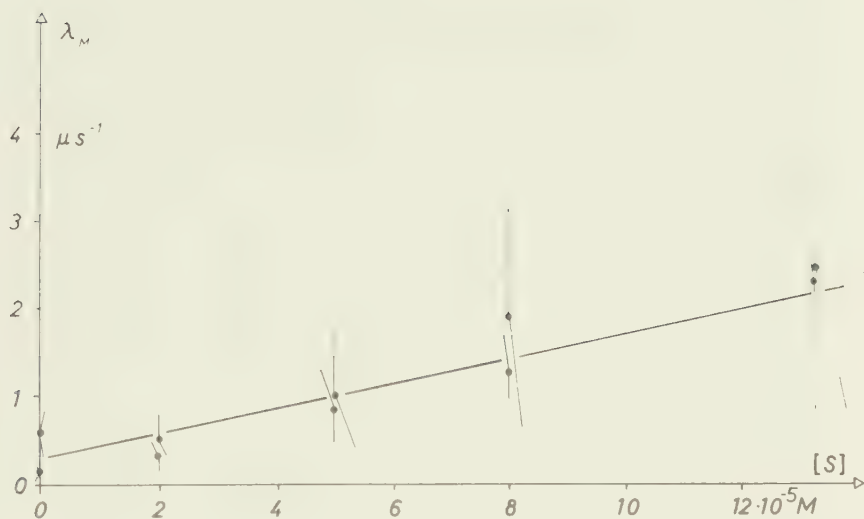


Fig.3.3: Relaxation rate of the muonium frequency as a function of solute concentration (fumaric acid).

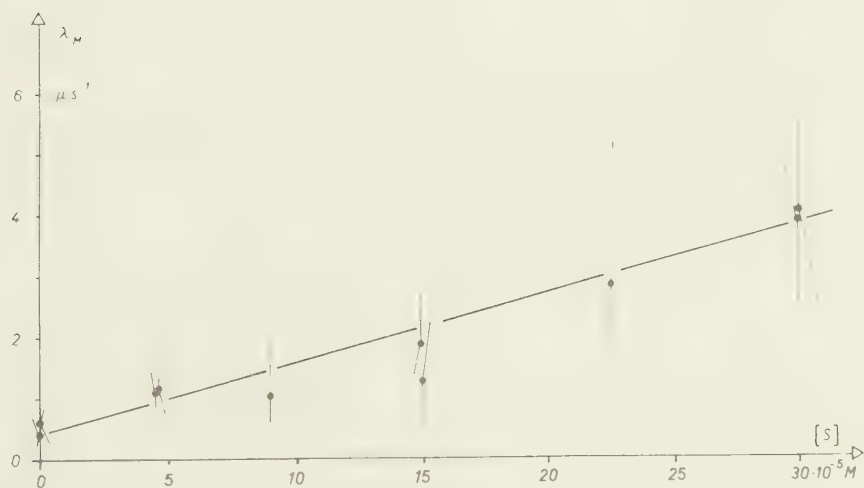


Fig.3.4: Relaxation rate of the muonium frequency as a function of concentration of maleic acid.

Table 3.1

A comparison of rate constants for Mu and H in aqueous solution at ambient temperatures.

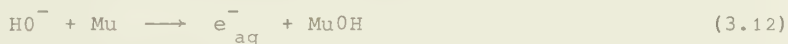
	$k_M^a)$ [M ⁻¹ s ⁻¹]	$k_H^a)$ [M ⁻¹ s ⁻¹]	$\frac{k_H}{k_M}$
<u>H abstraction:</u>			
methanol	$4.3 \cdot 10^5$	$2.5 \cdot 10^6$ [31]	≥ 80
ethanol	$6 \cdot 10^5$	$2.1 \cdot 10^7$ [31]	≥ 350
isopropanol	$8.0 \cdot 10^5$	$6.8 \cdot 10^7$ [31]	85
sec. butanol	$1.1 \cdot 10^6$	$1.3 \cdot 10^8$ [32]	120
formate ion (pH 7)	$7.8 \cdot 10^7$	$1.24 \cdot 10^8$ [33]	16
formic acid	$1 \cdot 10^8$	$4.5 \cdot 10^5$ [33]	4.5
<u>Br abstraction^{b)}</u>			
bromo-acetic acid	$1.5 \cdot 10^7$	$2.6 \cdot 10^8$ [32]	0.17
2-bromo-propionic acid	$4.0 \cdot 10^7$	$9.5 \cdot 10^8$ [34]	0.24
3-bromo-propionic acid	$2.7 \cdot 10^7$	$1.7 \cdot 10^8$ [34]	0.63
<u>addition^{b)}</u>			
maleic acid	$1.1 \cdot 10^8$	$6 \cdot 10^8$ [35]	0.06
fumaric acid	$1.4 \cdot 10^8$	$9 \cdot 10^8$ [35]	0.06
ascorbic acid	$1.8 \cdot 10^8$	$1.1 \cdot 10^9$ [35]	0.06
dihydroxy-fumaric acid	$4.5 \cdot 10^8$	$9 \cdot 10^7$ [35]	2
acetone	$8.7 \cdot 10^8$	$2.8 \cdot 10^8$ [36]	0.03
<u>inorganic solutes</u>			
MnO ₄ ⁻	$2.5 \cdot 10^8$	$2.4 \cdot 10^8$ [37]	1
Ag ⁺ b)	$1.6 \cdot 10^8$	$2.8 \cdot 10^8$ [38]	1.8
HO ⁻	$1.7 \cdot 10^8$	$1.5 \cdot 10^7$ [33]	1
NO ⁻	$1.5 \cdot 10^8$	$1.2 \cdot 10^8$ [39]	0.008
ClO ₄ ⁻	$5 \cdot 10^8$	nil [40]	-
F ⁻	$3 \cdot 10^8$	$1.5 \cdot 10^8$ [40]	-
Cl ⁻	$1 \cdot 10^8$	$< 10^5$ [39]	-
H ⁺	$1 \cdot 10^8$	$\approx 10^3$ [40]	-

a) this work, values are accurate to $\pm 10\%$

b) pH1 with HClO₄

c) derived from λ_0 in the pure alcohol

Similarly, reaction with formic acid and the formic acid ion is by H abstraction from the carbon atom. In brominated compounds halogen abstraction is highly favored over H abstraction [34]. Reaction with olefinic compounds proceeds by addition [1] and with acetone to 2/3 by H abstraction and to 1/3 by addition to the oxygen. For Mu it is likely to be primarily addition since this appears to be usually faster than for H, whereas abstraction is much slower for Mu than for H (the Mu adduct to acetone has been observed, see chapter 4.2). MnO_4^- and Ag^+ oxidize H atoms [41]. The high value for the corresponding rate constant indicates that this process occurs at a rate close to the diffusion controlled limit (compare $2k_H = 2 \cdot 10^{10} \text{M}^{-1} \text{s}^{-1}$ for the reaction $\text{H} + \text{H} \rightarrow \text{H}_2$ [41]). A unique reaction, i.e. generation of hydrated electrons, occurs with HO^- and with F^- [1]:



The reaction with NO_3^- is assumed to be



again by analogy with H [41].

Only upper limits of k_M could be determined for a number of substrates. Mu was clearly observed in pure methanol and ethanol, in 9M formic acid, 0.1M HClO_4 , 1.6M KF and in 5M HCl and NaCl. The corresponding k_M in table 3.1 were obtained by direct conversion of the measured λ_M , assuming a "concentration" of 24.7 M for methanol and 17.1 M for ethanol.

Quite often different literature values for k_H agree only within about one order of magnitude. More recent values were adopted in table 3.1.

A comparison of k_M with k_H (last column in table 3.1) reveals some dramatic isotope effects. Hydrogen abstraction by Mu appears to be much slower than for H, whereas Br abstraction is slightly faster. Except for dihydroxy-fumaric acid, Mu adds much faster than H. The rate of Mu addition to maleic and fumaric acid is probably close to the diffusion controlled limit. Regarding the size of these molecules it is plausible that this limit is lower than for the reaction with MnO_4^- and with Ag^+ . The span of isotope effects in the whole table exceeds two orders of magnitude in both the positive and the negative directions. Such large effects have been observed so far, only at low temperatures ($T < 200K$) for reactions where the isotope (H vs. D) is the species to be abstracted, but even at 77K there is no dramatic effect in the H abstraction from polyisobutylene when the isotope (H vs. D) is the attacking species [25].

3.3. Model Calculations

3.3.1. The Basic Formula

We shall confine ourselves to H abstraction reactions (3.3). These are the reactions which have been studied most extensively both experimentally and theoretically. Using 3.1 and separating the electronic and vibronic part of ΔE_o^* we obtain for the kinetic isotope effect

$$\frac{k_M}{k_H} = \underbrace{\frac{Q_{HMu}^*}{Q_{RHMu}}}_A \cdot \underbrace{\frac{Q_{Mu}}{Q_H}}_B \cdot \underbrace{\frac{\Gamma_H}{\Gamma_{Mu}}}_C \cdot \underbrace{\exp \left\{ \frac{E_{RHMu}^* - E_{HMu}^*}{kT} \right\}}_D \cdot \underbrace{\exp \left\{ \frac{\Delta E_o^*}{kT} \right\}}_E \cdot \underbrace{1}_{E1}$$

$\approx 1 \quad < 1 \quad \leq 1 \quad > 1 \quad \approx 1$

(3.14)

We now discuss the different terms:

A: In the approximation of separable degrees of freedom Q^* is a product of translational, rotational and vibrational contributions. Since R is an extended and heavy group, replacement of H by Mu in RHH leaves the mass and the moments of inertia of the activated complex almost unchanged. Whatever the values for the translational and rotational partition functions are, their isotopic ratios are unity to a good approximation. Vibrational frequencies of the activated complex depend strongly on isotopic substitution. At room temperature however, the corresponding partition functions are only slightly ($\leq 10\%$) greater than unity. Term A is therefore unity within a few percent.

B: This term is a ratio of translational partition functions for Mu and H. The respective gas phase values are proportional to $m^{3/2}$ so that the ratio becomes $1/27$. The gas phase expressions however are a poor approximation for the liquid, since they are derived for a free volume which is large compared with molecular dimensions. Reduction of the free volume results in an increase of the spacing between translational energy levels, and consequently in a decrease in the partition function. In the limit where this spacing is large compared to kT the partition functions, and so their ratio, approach unity. The true value for our system must lie between the two limits. An accurate value cannot be given without knowing more about the potential that is experienced by the hydrogen isotope in the solvent cage.

Support for $B \approx 1$ comes from the study of diffusion controlled reactions. In terms of activated complex theory, diffusion coefficients are proportional to the inverse one-dimensional translational partition function, i.e. to $m^{-1/2}$ [17]. If this expression gives the correct mass

dependence μ should diffuse three times faster than H. We see from the (most likely) diffusion controlled reactions of $\mu(H)$ with MnO_4^- , Ag^+ (table 3.1) that this is not the case. This is in agreement with the general observation that tracer diffusion in liquids is not sensitive to changes in tracer mass [42]. We may therefore conclude that the translational partition function of $\mu(H)$ in water is not severely mass dependent and that term B does not deviate strongly from unity.

- C: In the absence of tunneling we have $\Gamma_H = \Gamma_{\mu} = 1$. We shall show however that tunneling is important in both the reactions of μ and H and that the factor C may be significantly smaller than unity.
- D: This term gives the dependence of the kinetic isotope effect on the zero point vibrational energy. Because of the lighter mass of μ , $E_{RH\mu}^+$ is always greater than E_{RH}^+ and D takes a value larger than one.
- E: Within the Born-Oppenheimer (BO) approximation the electronic energy ($V(s)$ in fig. 3.1) is in the R_1/R_2 space the same for the two isotopic reactions. Significant deviations are expected in particular for molecules containing M1. The BO correction to the energy of atomic H(μ) in the ground state is

$$E - E_{\infty} = - \frac{e^2}{2\hbar^2} [\mu - \mu_{\infty}], \quad (3.15)$$

where μ is the true reduced mass of the electron-nucleus system and $\mu_{\infty} = m_e$ for infinite nuclear mass. For molecules it appears justified to approximate the correction to the BO energy by a sum of atomic contributions (3.15) as seen by a comparison with quantum chemical calculations (table 3.2).

Table 3.2

Corrections to the BO energy of simple molecules

	quantum chemical calculation, ref.[43] [cm ⁻¹]	sum of atomic corrections [cm ⁻¹]
H ₂	99.07 - 114.59 ^{a)}	116
HD	74.31 - 85.96 ^{a)}	88
D ₂	50.69	60
HMu	--	586

a) different calculations

This approximation may also hold for the activated complex so that the correction to the BO energy $V(s)$ is simply a parallel shift and to a first approximation does not contribute to the kinetic isotope effect, i.e. $E \sim 1$.

Equation (3.14) was derived for the gas phase and is applied here for reactions in aqueous solution. The reactants RH and H(Mu) as well as the activated complex are not very polar so that the effect of solvation on the reaction rate is expected to be small, in particular solvation should not contribute to the kinetic isotope effect.

The discussion of eq. (3.14) can be summarised as follows: Terms A and E are close to unity and need not be considered any longer. Term B is probably also not far from unity, but a reliable value cannot be assigned because of the lack of an appropriate theory of liquids. The terms C and D constitute the main contributions to the kinetic isotope effect and will be subject to model calculations. Whereas tunneling favors k_M over k_H the opposite is true for the effect of zero point vibrational energies.

3.3.2. The Model Barriers

Three different one-dimensional vibrational adiabatic barriers were used to calculate the kinetic isotope effects. They were all based on the unmodified BEBO potential $V(s)$ but differed in the contributions arising from zero point vibrational motion:

E(s)I : Johnston and Parr's [19] expressions for the force constants, which are derived for $s=s^\ddagger$, were assumed to hold all along the reaction path. The symmetric stretching and the twofold degenerate bending mode contribute to zero point vibrational energy.

E(s)II: This is analogous to E(s)I but only the symmetric stretching mode contributes to vibrational energy as is usually assumed in the case of collinear reactions [16].

E(s)III: The contribution of the vibrational energy is given by the empirical relationship [44]

$$\text{ZPE}(n) = 0.00598 [n \cdot \tilde{\nu}_1 + (1-n) \tilde{\nu}_2], \quad (3.16)$$

where ZPE is in kJ/mol, $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are the wave-numbers [cm^{-1}] for the stretching motion of R-H and H-H(Mu) respectively, and n is the bond order of the bond being broken.

All three barriers are continuous curves between the zero point vibrational energy levels of the reactant and the product. Their shapes and heights are slightly different. In general their maxima do not coincide with the maximum of $V(s)$, in particular not for Mu reactions. R was treated as a carbon atom of mass 12 (a larger mass does not influence the results seriously). 457.8 kJ/mol was taken for the H-H(Mu) bond energy D_{2s} , 570 N m^{-1} for the corresponding

force constant and $0.74 \text{ \AA}$ for the bond length. Whereas $1.09 \text{ \AA}$ was taken as the bond length of the single C-H bond in all reactions, the corresponding force constant was assumed proportional to the bond energy as in the Morse potential and calculated from the data for methane ($D_{1s} = 440 \text{ kJ/mol}$, $f = 504 \text{ N m}^{-1}$).

3.3.3. General Relation between Isotope Effect and C-H Bond Energy.

Figure 3.5 displays the predicted behaviour of the reaction probability per collision with the barrier

$$P = \Gamma \exp(-E_o^*/kT) \quad (3.17)$$

averaged over a Boltzmann distribution for the collision energy at 295 K. All three types of barriers lead to a decrease in P with increasing bond strength D_{1s} of the C-H bond. This is caused by a corresponding increase in the classical potential barrier V_b . Omission of the zero point energy from the bending modes (barrier II) causes an increase in P by roughly one order of magnitude. Barrier I and III lead to similar results for the H reaction.

Figure 3.6 shows the dependence of P_H/P_M on the C-H bond energy. With the assumption that the product of the terms A, B and E (3.14) is equal to one, P_H/P_M becomes directly the kinetic isotope effect k_H/k_M . It is predicted that Mu reacts much slower than H with strongly bonded H atoms, whereas for weakly bonded atoms it may well be the reverse. This means that for C-H bonds with $D_{1s} \geq 380 \text{ kJ/mol}$ (i.e. for the majority of C-H bonds) Mu abstracts with a much higher selectivity than H the most weakly bound hydrogen atom.

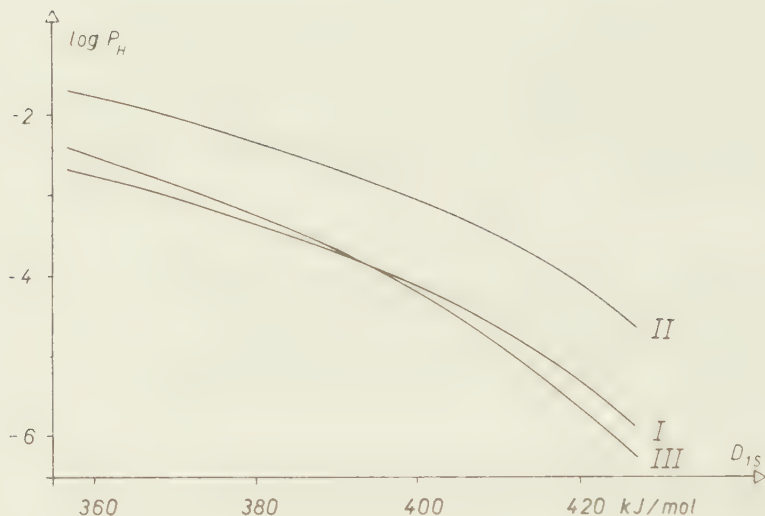


Fig.3.5: Reaction probability per collision for the reaction $H+RH \rightarrow H_2+R$ as a function of the R-H bond energy (295 K). The three curves are for the three different barriers.

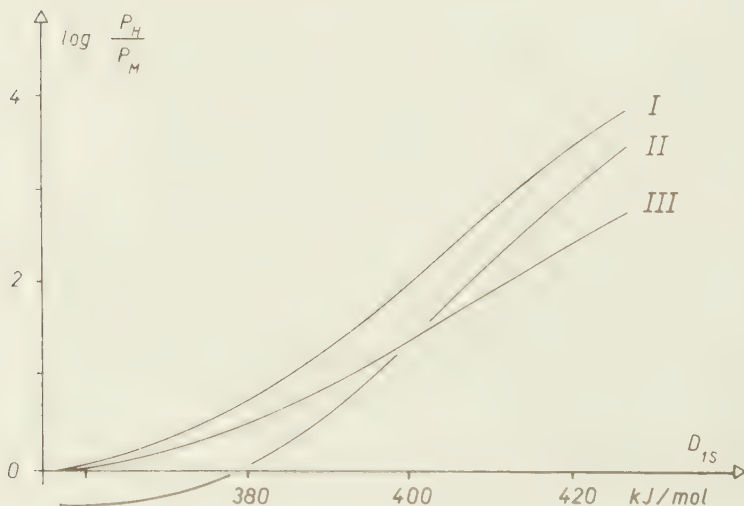


Fig.3.6: Isotope effect in the reaction probability per collision with the barriers I, II and III as a function of the R-H bond energy (295 K).

Table 3.3

Calculated tunneling factors and barrier heights for the reactions $R-H + Mu(H,D) \rightarrow R+H-Mu(H,D)$ using the vibrational adiabatic barrier $E(s)I$.

D_{1s} [kJ/Mol]	$\frac{Mu}{\Gamma(a)} E^\ddagger$ [kJ/mol]	$\frac{H}{\Gamma(a)} E^\ddagger$ [kJ/mol]	$\frac{D}{\Gamma(a)} E^\ddagger$ [kJ/mol]	Γ_H / Γ_{Mu}	$\exp \left\{ \frac{E_{RHMu}^\ddagger - E_{RHH}^\ddagger}{295 R} \right\}$			
427	5.8	59.8	2.7	35.9	2.1	34.0	0.46	17000
417	5.4	51.6	2.7	31.4	1.9	30.1	0.50	3770
410	4.8	46.0	2.6	28.8	1.8	27.7	0.54	1110
394	2.7	33.6	2.1	23.8	1.4	23.1	0.76	54
375	5.1	25.3	1.5	19.3	1.2	18.8	0.30	12
357	8.2	20.8	1.3	16.0	1.1	15.6	0.16	8

- a) Tunneling factors were obtained by numerical integration of eq. (3.2) using energy increments of $1/150$ of the barrier height.
 $\kappa(E)$ again was obtained numerically using the Numerov algorithm [29] and an increment in s of $0.01 \text{ \AA}$ in the mass weighted coordinate system.
 For $E > 1.7E_0^\ddagger$ κ was approximated by unity with an error $\lesssim 3\%$.

Table 3.3 gives a collection of numerical values for the tunneling factor and the vibrational adiabatic barrier height for the example of the barrier E(s)I. As expected the differences are much less between H and D than between H and Mu. Tunneling seems to be important, and the Mu reaction is in fact predicted to occur mainly by tunneling. On the other hand the increase in Γ on going from D to Mu is only moderate. This is so because the vibrational adiabatic barrier is much higher for the reaction of Mu. It is interesting to note the minimum in Γ_{Mu} at $D_{1s} \approx 394$ kJ/mol, whereas Γ_{H} and Γ_{D} decrease continuously with decreasing D_{1s} . The reason for this special behaviour of Γ_{Mu} is not clear. It may have to do with the de Broglie wavelength of the tunneling mass, which is of the order of the barrier dimension. All tunneling factors are very similar for the two barriers E(s)I and E(s)II, but considerably larger for the third one since E(s)III is narrower for the same height. Comparison of the last two columns in table 3.3 shows that the isotope effect is dominated by the zero point vibrational energy term (D in eq. 3.14), in particular for high values of D_{1s} .

3.3.4. Application to Specific Molecules

To correlate the experimental data with the calculations presented we use for the values of D_{1s} , the C-H bond dissociation energies by Egger and Cocks [45], corrected for the zero point vibrational energy of the C-H stretching mode. Since there are no data available on D_{1s} of the formate ion this is estimated from D_{1s} for formic acid (394 kJ/mol) using spectroscopic data ($\tilde{\nu}_{\text{C-H}} = 2943 \text{ cm}^{-1}$ for HCOOH [46], $\tilde{\nu}_{\text{C-H}} = 2803 \text{ cm}^{-1}$ for HCOO^- [47]). We assume a Morse potential which implies the proportionality of D_{1s}

with the corresponding force constant and with $(\tilde{\nu}_{\text{C-H}})^2$ and obtain $D_{1s} = 357 \text{ kJ/mol}$ for HC00^- .

In general we have to consider i sites of different reactivity for a molecule. The average reaction probability per collision of a hydrogen isotope with a C-H bond can be written by analogy to Baldwin and Walker [48]

$$\bar{P} = \frac{1}{\sum_i n_i} \cdot \sum_i n_i P_i, \quad (3.18)$$

where n is the number of equivalent C-H bonds. In the liquid state abstraction of the much stronger bound hydroxylic H has never been observed (see e.g. ref. [49]). The predicted selectivity for the reaction of hydrogen isotopes is shown in table 3.4 for the example of sec. butanol.

Table 3.4

Predicted selectivity of the reaction of hydrogen isotopes with sec. butanol at 295 K, based on barrier $E(s)I$.

	$\begin{array}{c} \text{OH} \\ \\ \text{H}_3\text{C} - \text{CH} - \text{CH}_2 - \text{CH}_3 \end{array}$			
$D_{1s} [\text{kJ/mol}]$	427	394	414.5	427
$n_i P_i (\text{D}) \left\{ \begin{array}{l} \text{absolute} \\ \% \end{array} \right.$	$3 \cdot 0.20 \cdot 10^{-5}$ 3.8	$0.12 \cdot 10^{-3}$ 75.0	$2 \cdot 0.14 \cdot 10^{-4}$ 17.4	$3 \cdot 0.20 \cdot 10^{-5}$ 3.8
$n_i P_i (\text{H}) \left\{ \begin{array}{l} \text{absolute} \\ \% \end{array} \right.$	$3 \cdot 0.12 \cdot 10^{-5}$ 2.2	$0.13 \cdot 10^{-3}$ 79.8	$2 \cdot 0.13 \cdot 10^{-4}$ 15.8	$3 \cdot 0.12 \cdot 10^{-5}$ 2.2
$n_i P_i (\text{Mu}) \left\{ \begin{array}{l} \text{absolute} \\ \% \end{array} \right.$	$3 \cdot 0.17 \cdot 10^{-9}$ 0.02	$0.33 \cdot 10^{-5}$ 99.0	$2 \cdot 0.17 \cdot 10^{-7}$ 1.0	$3 \cdot 0.17 \cdot 10^{-9}$ 0.02

The table illustrates the much higher selectivity that is predicted for the reaction of Mu. Unfortunately, there is no way to measure this effect for Mu, and the difference between H and D is rather small. The numbers of interest are the ratios of average reaction probabilities per colli-

Table 3.5

Isotope effect in the reaction probability per collision of a hydrogen isotope with the substrate molecule at 295 K and comparison with experimental values.

	$\overline{P}_D / \overline{P}_H$ a)			k_D / k_H b)		$\overline{P}_H / \overline{P}_M$ a)			k_H / k_M c)	
	E(s) I	E(s) II	E(s) III	exp.	E(s) I	E(s) II	E(s) III	exp.		
methanol	1.20	1.00	1.00	1.50	1800	545	177		≥ 80	
ethanol	1.09	0.94	0.94	1.85	606	160	81		≥ 350	
isopropanol	0.96	0.83	0.85	0.62	42	9	12		85	
sec. butanol	0.98	0.84	0.85		49	11	14		120	
formate ion	1.00	0.74	0.95		1.1	0.4	0.9		16	
formic acid	0.92	0.79	0.83		39	8	12		≥ 4.5	

a) $\overline{P}_i / \overline{P}_j = k_i / k_j$, if the product of the terms A, B and E (3.14) is unity

b) Ref. [50]

c) Table 3.1

sion, which give directly the kinetic isotope effect if the product of the terms A, B and E (3.14) is equal to one. From the values in table 3.4 we obtain $\bar{P}_D/\bar{P}_H$ ($\approx k_D/k_H$) = 0.98 and $\bar{P}_H/\bar{P}_M = 49$, i.e. there should be no isotope effect between H and D, but a large one between Mu and H. The increase in tunneling for H as compared to D compensates for the increased barrier height. The same behaviour is predicted roughly for all substances and all three types of barriers (table 3.5) except for H vs. Mu in the reaction with the formate ion where only a small isotope effect is predicted. Barrier E(s)I yields the best prediction of the experimental isotope effect although it seems to be difficult to account for the full effect. It is confirmed that Mu is a much more sensitive probe than D to test reaction rate theories.

3.3.5. A Modified BEBO Barrier

Only one of the reactions considered here has been investigated over a wide temperature range. It is the reaction of H with methanol for which experimental data exist between 125 K and 575 K (fig. 3.7). The data points form a surprisingly continuous curve across the two phase transitions between solid matrix, liquid and gas. Data points for the reaction of Mu represent only upper limits. They are obtained from the relaxation rates of Mu in pure methanol (taken as 24 M solution) assuming that the whole relaxation rate stems from chemical reaction.

The rate constant may be represented by an Arrhenius type expression

$$k = A \cdot \Gamma \exp(-E_O^+/RT), \quad (3.19)$$

where A is taken as a temperature independent adjustable

parameter. The barriers used so far can simulate quite well the high temperature data (i.e. the barriers have approximately the right height) but they do not give enough curvature in the Arrhenius plot (i.e. the barriers are too wide and do not allow for enough tunneling). To get agreement between theoretical and experimental points of the H reaction we scale the width of the potential barrier $V(s)$ by changing Pauling's constant C (3.4) from 0.26 to 0.15. This reduces the width of the barrier but leaves its height unaltered. The zero point vibrational contribution to the barrier is as for $E(s)$ II. The solid curves in fig. 3.7 represent the calculated rate constants using an A factor of $2.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for both reactions (experimental values: $A = 6.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [51], $3.8 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [52] for the gas phase and $A = 2.5 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the solid matrix. We see that this barrier can also account for the Mu data.

Fig.3.8 displays the potential energy and the vibrational adiabatic barrier as a function of the reaction coordinate s in a skewed, mass weighted coordinate system [17] where the effective mass is independent of s ($m^* = 1.71 \text{ u.}$ for H+methanol, 1.02 u. for Mu+methanol). A selection of the tunneling factors is given in table 3.6.

Table 3.6

Calculated tunneling factors for the reactions $\text{H}(\text{Mu}) + \text{methanol}$ at different temperatures.

Reaction	E_0^+ [kJ/Mol]	Γ (T)				
		595	495	395	295	195 K
$\text{H} + \text{CH}_3\text{OH}$	20.6	1.8	2.2	3.2	6.8	56
$\text{Mu} + \text{CH}_3\text{OH}$	34.4	2.8	4.2	9.1	52	7200

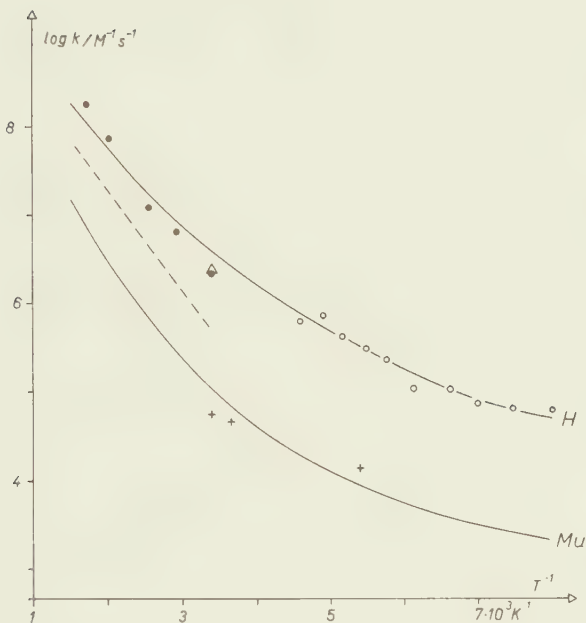


Fig.3.7: Experimental and theoretical Arrhenius plots for the reaction of H(Mu) with methanol.

k_H : • gas phase [51]
 --- gas phase [52]
 Δ solution [31]
 o solid matrix [53]
 k_{Mu} : + this work

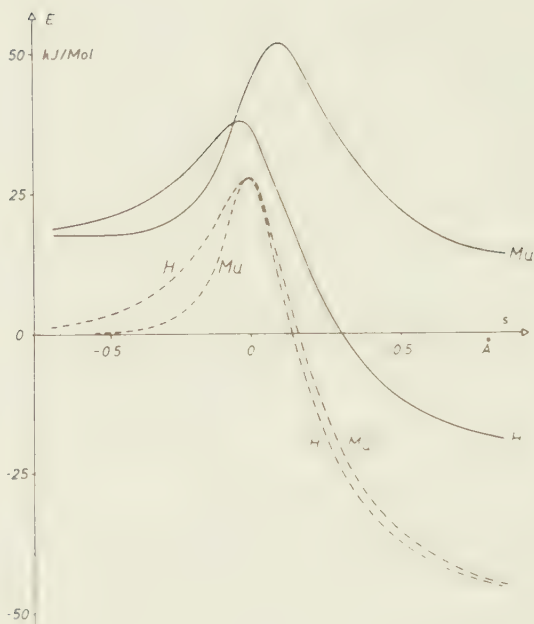


Fig. 3.4: Potential barrier for the reaction of H(Mu) with methanol.

- potential energy along s in a skewed, mass weighted coordinate system. Modified BEBO potential.
- vibrational adiabatic energy analogous to $E(s)$ II.

We note the increased importance of tunneling as compared to the unmodified barrier. Also tunneling is a strong function of temperature. This is particularly true for the reaction of Mu despite the fact that the corresponding vibrational adiabatic barrier is quite wide at its base because of the almost thermoneutral reaction.

3.4. Discussion

Some of the experimental values for k_M (table 3.1) can be compared with earlier data. Brewer et al. [9] report $3.8 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and Minaichev et al. [54] $1.2 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction with ClO_4^- (this work: $k_M < 5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$). Similarly the reported values for the reaction with nitrate are $1.3 \cdot 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ [9] and $1.7 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [54] as compared to $1.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in this work. For the reaction with HO^- ($k_M = 1.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and with H^+ ($k_M < 10^5 \text{ M}^{-1} \text{ s}^{-1}$) the literature values are $1.8 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $6 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ respectively [54]. Thus, there is a disagreement by orders of magnitude. The earlier data were obtained by an indirect method employing analysis of the total spin polarization of muons in a diamagnetic environment, P_D (the residual polarization), for various solute concentrations. The values of k_M are then strongly model dependent. The analysis of Minaichev et al. [54] implied a very high relaxation rate for Mu in water ($\lambda_M = 1.6 \cdot 10^{10} \text{ s}^{-1}$) which is clearly invalidated by the direct observation of Mu in water ($\lambda_M \approx 2.5 \cdot 10^6 \text{ s}^{-1}$, compare fig. 2.4). Brewer et al. adopted a value of $P_M = 0.45$ whereas we find $P_M \approx 0.20$. Furthermore, it has been pointed out [55] that the large number of free parameters inherent in the model may have led to non-exclusive fits. Meanwhile it has been shown for NO_3^- [11, 56] that

residual polarization studies based on the appropriate model lead to good agreement with the directly determined value of k_M .

The fact that there is little or no isotope effect in the reactions with MnO_4^- and with Ag^+ , which are probably diffusion controlled, supports the validity of the Stokes-Einstein law which predicts a mass independent relation between diffusion coefficient and solvent viscosity. Other theories predict a $m^{-1/2}$ dependence [42].

It is important not to overestimate the significance of the numerical results from the model calculations presented. The assumptions of a three body problem, collinearity, one-dimensionality, the neglect of curvilinear effects, the improper treatment of the liquid state and the assumptions inherent in the BEBO treatment and in transition state theory are rather crude approximations. The extent to which they falsify the result is hard to estimate. In this view the agreement between experiment and theory appears surprisingly good. For the case of the temperature dependence of k_H in the reaction with methanol (fig.3.7) this agreement was achieved by scaling the barrier width. Application of this modified barrier to calculate the isotope effects of the other reactions gives poor results (too small isotope effects are predicted). Introduction of a temperature dependent A-factor in equation (3.19) instead of a reduced barrier width can probably also lead to satisfying agreement with experiment.

Despite the limitations of the model it is believed that the following qualitative conclusions can be made:

- The effective barrier is quite different in height and width for the reaction of different isotopes.
- Barriers based on the principle of vibrational adiabaticity can reproduce experimental effects quite satis-

factory. (For a long time it has been customary to exclude zero point energies and use the classical barrier $V(s)$ to calculate tunneling corrections. Such an approach results in an enormous increase in Γ for the Mu reaction and predicts $k_M \gg k_H$.)

- The isotope effect k_H/k_M in the H abstraction reactions is governed by zero point vibrational energies in the activated complex. This effectively reduces k_M and at the same time suppresses the influence of tunneling. Still H abstraction by Mu at room temperature occurs predominantly by tunneling.

Br abstraction and Mu addition to unsaturated compounds have not been treated theoretically. Here k_M is usually much greater than k_H . It is therefore believed that isotope effects are governed by tunneling. This is in agreement with the prediction (table 3.3) that for low barriers zero point vibrational effects cannot compensate for the increase in the reaction rate due to tunneling. Kelley et al. [26] who have investigated addition of hydrogen isotopes to olefins also favor tunneling as the relevant mechanism for these reactions.

In conclusion we feel that further comparison of rate constants for bimolecular reactions of Mu, H and D, and in particular of their temperature dependencies, could be very fruitful. This has been demonstrated for the reaction of H, Mu with F_2 in the gas phase, where good agreement between experiment [57] and theory [58] has been obtained.

4. MUONIUM SUBSTITUTED FREE RADICALS

Over 15 years ago it was postulated by A.M. Brodskii [59] that Mu may add to unsaturated molecules such as ethylene to form muonic radicals (reaction 1.2). Since then, much effort in different laboratories has been devoted to low (≤ 10 G) transverse field μ SR experiments in the search for these species, however, with no success. The reason for this non-observation lies in the neglect of a term in the Hamiltonian describing the system. A muonic radical was viewed as a two-spin system analogous to Mu, but with a reduced hyperfine coupling constant [55]. Consequently, the muonium precession frequency was sought in low fields, but with larger splitting than that of Mu at higher fields. However, in most organic radicals additional magnetic nuclei, e.g. protons, are coupled to the unpaired electron. They cause a distribution of the muon polarization over many frequencies, in particular for intermediate and low fields.

In this chapter the theory is developed for a basic understanding of muonic radicals. Numerical calculations lead to exact results for all fields, but approximate methods are more convenient and transparent and yield sufficiently accurate results for most situations where radicals are actually observed. First experimental results are given and discussed.

4.1. Theory

4.1.1. Hamiltonian and Eigenfunctions

In accordance with convention we define the z-direction of an cartesian coordinate system to be parallel to the external field B and the x-direction parallel to the muon polarization of the beam. The Hamiltonian for muonium

substituted radicals in liquids is in frequency units:

$$\hat{H} = \nu_e \hat{S}_z - \nu_\mu \hat{I}_z^\mu - \sum_k^K \nu_k \hat{I}_z^k + A_\mu \hat{S} \cdot \hat{I}^\mu + \sum_k^K A_k \hat{S} \cdot \hat{I}^k, \quad (4.1)$$

where ν_e , ν_μ and ν_k are the Larmor precession frequencies for the electron, muon and the k 'th nucleus ($\nu_e = 2802.47$ kHz/G for $g = g_e$, $\nu_\mu = 13.55$ kHz/G and $\nu_k = 4.258$ kHz/G for protons). A_μ and A_k , the isotropic hyperfine coupling constants (hfcc's), are direct measures of the electron spin densities at the corresponding nuclei. Anisotropic contributions to the hyperfine interaction arising from direct dipole-dipole interaction are averaged to zero due to rapid tumbling of the molecules [60]. Similarly, we employ the isotropic g -value for the unpaired electron which, however, may deviate slightly from g_e , the value for the free electron. For all radicals except those where the unpaired electron occupies a degenerate state (e.g. $\text{MuO}\cdot$) the orbital momentum is quenched [61]. Furthermore, coupling between different nuclei is small ($|J| \leq 20\text{Hz}$ for most protons) and can be neglected for our purposes.

We write the normalized eigenkets to $\hat{H}$ (4.1)

$$|n\rangle = \sum_i c_{ni} |X_i\rangle \quad (4.2)$$

expanded in the basis of product spin functions

$$|X_i\rangle = |X_i^\mu\rangle |X_i^e\rangle \prod_N |X_i^k\rangle, \quad (4.3)$$

which are eigenkets to the Zeeman Hamiltonian

$$\hat{H}_Z = \nu_e \hat{S}_z - \nu_\mu \hat{I}_z^\mu - \sum_k^K \nu_k \hat{I}_z^k. \quad (4.4)$$

(Note that the indices e , μ and k appear as subscripts on frequencies and as superscripts on wavefunctions, operators and quantum numbers.)

4.1.1. Evolution of Spin Polarization in Multi-Spin Systems

In this chapter we present the theory [62] for the evolution of μ^+ spin polarization in an environment characterized by any multi-spin Hamiltonian. The formalism applies not only to muonic radicals in liquids, but also to muonic U_2 -centers in solids or similar paramagnetic species. Several existing theories are restricted to two-spin systems (electron, muon), neglecting magnetic interaction of the muon with other nuclei, or including them only phenomenologically in the form of a relaxation parameter. Beck, Meier and Schenck [63] formulated the problem for multi-spin systems in longitudinal fields. We start with a similar approach, but introduce a formalism which allows an enormous reduction in high dimensional matrices and leads to more practical equations for numerical evaluation. These equations are more transparent than earlier ones, we consider, and demonstrate the close relationship between μ SR and magnetic resonance.

First we consider the case where the muon-electron-nuclear system starts out at $t=0$ with a muon polarization given by the beam polarization P . The observable evolution of polarization in an arbitrary direction q defined by the observation axis of the positron counter telescope is

$$P_q(t) = \langle \hat{\sigma}_q \rangle = \text{Tr}\{\hat{\rho}(t) \cdot \hat{\sigma}_q\}, \quad (4.5)$$

where $\hat{\rho}$ is the density operator of the combined system and $\hat{\sigma}_q$ is the muon Pauli spin operator. To solve equation (4.5) one may start with the equation of motion

$$\dot{\hat{\rho}} = -\frac{1}{2\pi} [\hat{H}, \hat{\rho}], \quad (4.6)$$

and then write out the commutator to obtain a set of coupled differential equations for the components of the muon and electron polarizations and their cross correlations. This method was used by Nosov and Yakovleva [64]

and has been adapted by others [65 - 67] to include diverse chemical reactions. Alternatively, one may rewrite (4.5) in the Heisenberg representation

$$P_q(t) = \text{Tr}\{\hat{\rho}(0) \cdot \hat{\sigma}_q(t)\}, \quad (4.7)$$

$$\hat{\sigma}_q(t) = \exp(i2\pi\hat{H}t)\hat{\sigma}_q\exp(-i2\pi\hat{H}t)$$

and evaluate (4.7) directly in the eigenbasis (4.2) of $\hat{H}$:

$$P_q(t) = \sum_{m,n} \langle n | \hat{\rho}(0) | m \rangle \langle m | \hat{\sigma}_q | n \rangle \exp(i\omega_{mn}t), \quad (4.8)$$

where $\omega_{mn} = \hbar^{-1}(E_m - E_n)$. $\hat{\sigma}_q$ and $\hat{\rho}(0)$ are square matrices of dimension $4\prod_k(2I^k+1)$, but may be written as tensor products of single-spin matrices

$$\begin{aligned} \hat{\sigma}_q &= \hat{\sigma}_q^\mu \otimes \underline{1}^e \otimes \prod_k \underline{1}^k \\ \hat{\rho}(0) &= \hat{\rho}^\mu(0) \otimes \hat{\rho}^e(0) \otimes \prod_k \rho^k(0) \\ &= \hat{\rho}^\mu(0) \otimes \frac{1}{2} \underline{1}^e \otimes \frac{1}{\prod_k (2I^k+1)} \underline{1}^k \end{aligned} \quad (4.9)$$

for the case that electron and nuclear spins are initially uncorrelated with the muon spin, i.e. unpolarized. This method has been used by Beck et al. [63] and by Percival and Fischer [55]. The disadvantage is that it is necessary to introduce several unitary transformations in the full dimension of the matrices, which grow by a factor of $(2I^k+1)$ for each additional nucleus. This becomes extremely impractical with an increasing number of spins. To reduce the problem we note that the initial muon density operator $\rho^\mu(0)$ is expressed conveniently in a basis corresponding to quantization of the spins along the direction of the beam polarization, and $\hat{\sigma}_q^\mu$ in a basis corresponding to quantization in the direction of observation

$$\begin{aligned}\hat{\rho}_{(0)}^{\mu} &= \frac{1}{2} \begin{pmatrix} 1+P & 0 \\ 0 & 1-P \end{pmatrix} = \frac{1}{2} \left\{ 1^{\mu} + P \cdot \hat{\sigma}_b^{\mu} \right\} \\ \hat{\sigma}_q^{\mu} &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},\end{aligned}\quad (4.10)$$

provided that no evolution of the spin has occurred before formation of the species. Using (4.9, 4.10) in (4.7) results in

$$P_q(t) = \frac{1}{4\prod_k (2I^k+1)} \cdot \text{Tr} \left\{ \hat{\sigma}_q(t) + P \cdot \hat{\sigma}_b \cdot \hat{\sigma}_q(t) \right\} \quad (4.11)$$

and since $\text{Tr} \hat{\sigma}_q(t) = 0$

$$P_q(t) = \frac{P}{4\prod_k (2I^k+1)} \cdot \text{Tr} \left\{ \hat{\sigma}_b \cdot \hat{\sigma}_q(t) \right\}. \quad (4.12)$$

Usually (4.12) has to be evaluated for the special case of $\hat{\sigma}_b = \hat{\sigma}_q$ ($b = q = z$ for longitudinal field experiments, $b = q = x$ for transverse field), i.e.

$$P_q(t) = \frac{P}{4\prod_k (2I^k+1)} \sum_{m,n} |\langle m | \hat{\sigma}_q | n \rangle|^2 \exp(i\omega_{mn} t). \quad (4.13)$$

Thus, the magnitude of the muon polarization that oscillates at frequency ω_{mn} is proportional to the transition moment between the two states $|\langle m | \hat{\sigma}_q | n \rangle|^2$. The same expression occurs for the intensity of a magnetic dipole transition in magnetic resonance, demonstrating the close relationship between the two techniques.

In order to evaluate the magnitude of the muon polarization that oscillates at ω_{mn} it is convenient to use the basis of product functions. Inserting (4.2, 4.3) in (4.13) we obtain

$$\begin{aligned}|P_z^{mn}| &= \frac{P}{4\prod_k (2I^k+1)} \left| \sum_{i,j} c_{ni} c_{mj} \langle \chi_i^{\mu} | \hat{\sigma}_z | \chi_j^{\mu} \rangle \delta_{ij} \prod_k \delta_{ij}^k \right|^2 \\ &= \frac{P}{\prod_k (2I^k+1)} \left| \sum_j c_{nj} c_{mj} m_j^{\mu} \right|^2,\end{aligned}\quad (4.14)$$

and

$$|P_x^{mn}| = \frac{P}{4 \prod_k (2I^k + 1)} \left| \sum_{i,j} c_{ni} c_{mj} \langle \chi_i^u | \hat{\sigma}_x | \chi_j^u \rangle \delta_{ij}^e \prod_k \delta_{ij}^k \right|^2 \quad (4.15)$$

The presence of $\delta_{ij}^{e,k}$ results in the vanishing of many matrix elements with concomitant saving of computing time.

The derivation of formulae (4.10-15) holds for the case where the fraction of muon polarization in the radical is identical with the fraction of muons in these radicals, i.e. where no polarization has been lost during formation of the species. Loss of polarization occurs if the rate of formation is of the same order or slower than the frequency differences between the observed species and its precursor. Extension of these formulae to include chemical reactions is straightforward. Expressions given by Percival and Fischer [55] simply must be translated into the formalism used here.

Consider for example the case where Mu has been formed at time zero with probability h_{Mu} and reacts with a rate λ_1 to form a radical, which thereafter decays with a rate λ_2 to form products. Before reaction, the polarization oscillates with ω_{lj}^{Mu} between the muonium states l,j in a transverse field. We wish to calculate the polarization at each radical frequency ω_{mn}^R after all Mu has reacted ($\lambda_1 t \gg 1$). We find for P ($P(R_2)$ in table 4, ref. [55]):

$$P_x(t) = h_{Mu} \lambda_1 e^{-\lambda_2 t} \sum_{ljmn} W_{ljmn} [\lambda_1 - \lambda_2 + i(\omega_{mn}^R - \omega_{jl}^{Mu})]^{-1} e^{i\omega_{mn}^R t} \quad (4.16)$$

with

$$\begin{aligned} W_{ljmn} &= \langle m | 1 \rangle \langle 1 | \hat{\rho}_{(0)}^{Mu} | j \rangle \langle j | n \rangle \langle n | \hat{\sigma}_x | m \rangle \frac{1}{\prod_k (2I^k + 1)} \\ &= \langle m | 1 \rangle \left\{ \langle 1 | j \rangle + \langle 1 | \hat{\sigma}_x | j \rangle \right\} \langle j | n \rangle \langle n | \hat{\sigma}_x | m \rangle \frac{1}{\prod_k (2I^k + 1)} \quad (4.17) \end{aligned}$$

In general the Mu eigenstates $|l\rangle$, $|j\rangle$ have to be written in the same dimension as the radical states $|n\rangle$, $|m\rangle$, i.e. one has to include all uncoupled nuclei. Only in the high field limit, where the radical nuclei are decoupled from the electron, and the radical frequencies degenerate to two lines only (see Section 4.1.6.), one can neglect these nuclei and write all wavefunctions in the basis of electron-muon product functions. It is primarily in the high field region that polarization at radical frequencies is being studied quantitatively [68] but a first result has also been obtained for the absence of an external field (section 4.2).

4.1.3. Selection Rules for μ SR Transitions

In zero field the Zeeman terms in (4.1) vanish. The remainder of $\hat{H}$ commutes with $\hat{F}^2$ and $\hat{F}_z$ ($\hat{F} = \hat{S} + \hat{I}^l + \sum \hat{I}^k$). The eigenfunctions in low fields ($v_e \ll A_\mu, A_k$) are therefore characterized to a good approximation by the quantum numbers F_τ, M_F , where τ distinguishes between states of different energies but equal F, M_F .

The intensity of a μ SR transition is proportional to the square of the corresponding matrix element (4.13)

$$| \langle F'_\tau, M'_F | \hat{O}_q | F_\tau, M_F \rangle |^2 \quad (4.18)$$

Here, $q=0$, i.e. $\hat{O}_q = \hat{O}_z$ for longitudinal, and $q = \pm 1$, i.e. $\hat{O}_q = \frac{1}{2} (\hat{O}_+ + \hat{O}_-) = \hat{O}_x$ for transverse field experiments. For $F' = F (\Delta F=0)$ we see that (4.18) differs from zero only if

$$\Delta M_F = 0 \quad (4.19)$$

in low longitudinal field, and

$$\Delta M_F = \pm 1 \quad (4.20)$$

in low transverse field experiments. To deduce the complete

selection rules we use the Wigner-Eckart theorem, which states [ref. 69, p.489]

$$\langle F'_{\tau}, M'_{\tau} | \hat{\sigma}_q | F_{\tau}, M_{\tau} \rangle = \frac{1}{\sqrt{2F'_{\tau}+1}} \langle F'_{\tau} | \hat{\sigma}_q | F_{\tau} \rangle \langle F, 1, M_F, q | F', M_F' \rangle. \quad (4.21)$$

For a non-vanishing transition neither the reduced matrix element $\langle F'_{\tau} | \hat{\sigma}_q | F_{\tau} \rangle$ (which is a continuous function) nor the Clebsch-Gordan coefficient $\langle F, 1, M_F, q | F', M_F' \rangle$ (which is a quantized factor) may vanish. The latter condition requires [ref.69, p.478]

$$M_F' = M_F + q, \text{ i.e. } \Delta M_F = q \quad (4.22)$$

with $q=0$ in longitudinal fields and $q=\pm 1$ in transverse field experiments, and simultaneously

$$|F-1| \leq F' \leq F+1, \text{ i.e. } \Delta F = 0, \pm 1 \quad (4.23)$$

These are the selection rules sought for transitions in low magnetic field.

In high fields ($v_e \gg A_{\mu}, A_k$) the eigenfunctions to $\hat{H}$ become pure product functions (4.3) because of decoupling of the spins. Therefore, they are characterized by the z-components of the individual angular momenta, m^s, m^{μ}, m^k . The transition operator $\hat{\sigma}_q$ acts upon the muon wavefunction only, and the simple high field selection rules

$$\Delta m^{\mu} = q, \quad \Delta m^s = \Delta m^k = 0 \quad (4.24)$$

readily are obtained from (4.13).

In intermediate fields neither F nor the individual m^i are good quantum numbers. $\hat{H}$ mixes product functions of equal $M = \Sigma m^i$. Thus M characterizes a wavefunction partly. Because of

$$|\hat{\sigma}_q | M \rangle = |M+q \rangle \quad (4.25)$$

matrix elements of the form $\langle M' | \hat{\sigma}_q | M \rangle$ are in general non-zero for

$$\Delta M = q. \quad (4.26)$$

It is only in high fields that the allowed transitions necessarily have considerable intensity, since then they occur between pure product states. In intermediate and zero fields the intensities depend upon several terms which are products of the expansion coefficients corresponding to the relevant product functions. Accidental cancellation of terms may occur.

4.1.4. Number of Allowed Transitions

The total intensity of a μ SR spectrum is limited by the total asymmetry corresponding to the beam polarization. We are therefore interested in the number of transitions between which this polarization is shared.

In transverse fields high enough so that we have essentially pure product states (4.1) the number of transitions equals the number of different combinations of electron and nuclear (not counting the muon) spins. This is half the total number of available states, i.e. $2 \prod_k (2I_k + 1)$. The number of distinguishable frequencies may be less if some of the spins are equivalent, and in the high field limit it is only two since all transitions corresponding to different combinations of nuclear spins degenerate. In high longitudinal fields there are no allowed transitions.

No convenient closed expressions were found for the number of transitions in intermediate or zero field for general spin systems. We shall therefore confine ourselves to the case of N spin- $\frac{1}{2}$ particles, including electron and muon. The secular determinant of dimension 2^N factorises according to $M = \sum m_i$ into subdeterminants of dimension

$$D = \frac{N!}{\left(\frac{N}{2} + M\right)! \left(\frac{N}{2} - M\right)!} = \left(\begin{matrix} N \\ \frac{N}{2} - M \end{matrix} \right). \quad (4.27)$$

Transitions are allowed from all states belonging to M to all states belonging to $M' = M+q$ (4.26). Thus, we count the number of transitions in intermediate transverse fields ($q = \pm 1$)

$$Q_{\perp}^{\pm 1} = \binom{N}{0} \binom{N}{1} + \binom{N}{1} \binom{N}{2} + \dots + \binom{N}{N-1} \binom{N}{N} = \binom{2N}{N-1}. \quad (4.28)$$

Similarly we obtain the number of transitions in intermediate longitudinal fields ($q = 0$)

$$\begin{aligned} Q_{\parallel}^{\pm 1} &= \frac{1}{2} \binom{N}{0} \left[\binom{N}{0} - 1 \right] + \frac{1}{2} \binom{N}{1} \left[\binom{N}{1} - 1 \right] + \dots + \frac{1}{2} \binom{N}{N} \left[\binom{N}{N} - 1 \right] \\ &= \frac{1}{2} \left\{ \left[\binom{N}{0} \right]^2 + \left[\binom{N}{1} \right]^2 + \dots + \left[\binom{N}{N} \right]^2 \right\} - 2^N \\ &= \frac{1}{2} \left\{ \binom{2N}{N} - 2^N \right\}. \end{aligned} \quad (4.29)$$

Thus for a muonic radical with four protons coupling we get $Q_{\perp}^{\pm 1} = 792$ and $Q_{\parallel}^{\pm 1} = 430$. Although some of the transitions carry more intensity than others, it is easily imagined that distribution of polarization over so many frequencies renders the detection of radicals difficult under these conditions.

In the absence of an external field all states belonging to the same F_{τ} are degenerate. Thus many of the transitions coincide in frequency, resulting in a simplification of the spectrum. The derivation of a convenient formula for the number of different frequencies ($\nu \neq 0$) is lengthy and only the result [70] is given here,

$$Q^0 = \frac{3}{2(N+2)} \binom{2N}{N-1} - \frac{1}{2} \binom{N}{N/2 - n}, \quad (4.30)$$

with $n=1$ for even N and $n=\frac{1}{2}$ for odd N . It may be noted that a significant fraction of polarization does not oscillate ($\nu = 0$). It is easily confirmed that the selection rules (4.22) for longitudinal field ($q = 0$) and for

transverse field ($q = 1$) lead to the same result for Q^0 . For a muonic radical with four inequivalent protons coupling we find $Q^0 = 141$. Equivalence of spins results in further reduction of the number of different frequencies (section 4.1.7.).

4.1.5. Numerical Example

A computer program was written in FORTRAN to calculate eigenvalues and eigenvectors to $\hat{H}$ and to evaluate intensities based on equation (4.15). It can handle $N = 6$ spin- $\frac{1}{2}$ particles using 64000₈ core memory. We realize, however, that it is quite inefficient in its present state. Instead of factorizing the secular determinant according to M (4.25) and taking advantage of the equivalence of spins the entire determinant of dimension 2^N is diagonalized. Also the evaluation of (4.15) is inefficient. Still it proved very useful to yield quantitative predictions of μ SR spectra.

It is instructive to discuss the results on the transverse field example of a simple muon-electron-proton system with typical coupling constants. In the Breit-Rabi type diagram (fig.4.1, compare fig.1.1 for Mu) above ≈ 100 G all energies are essentially linear in B, i.e. the states are practically pure product states. It is clear that the low field muonium frequency, $\nu_- = \frac{1}{2} (\nu_e - \nu_\mu) = 1.394$ MHz/G, cannot occur. However, analogous transitions exist with $\Delta M_F = \pm 1$ within $F = \frac{3}{2}$ (see also fig. 4.2). They are degenerate at $\nu = \frac{1}{4} (\nu_e - \nu_\mu - \nu_p) = 0.93$ MHz/G below ≈ 5 G. The allowed transitions are displayed in fig. (4.2), and their calculated Fourier amplitudes are shown in line form in fig. (4.3) where the total polarization in the radical is normalized to unity.

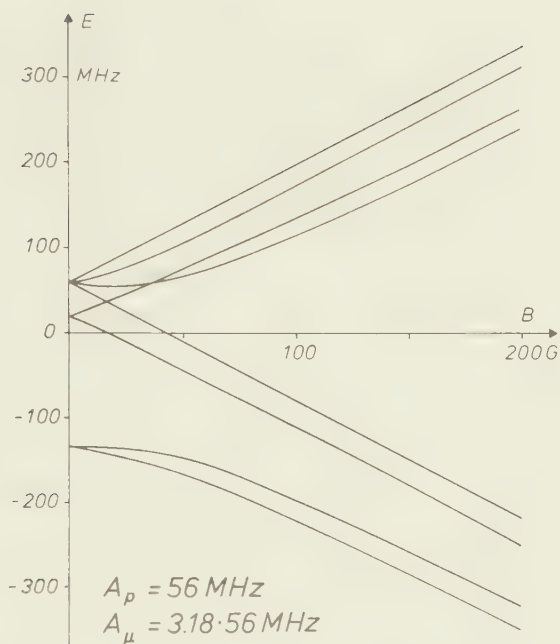


Fig.4.1: Energy diagram for a muonic radical with a single proton coupling.

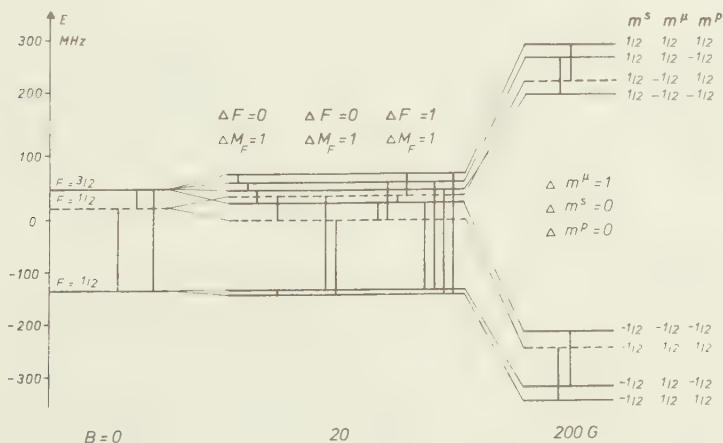


Fig.4.2: μSR transitions in a $\mu\text{-e-p}$ system in zero, intermediate and high transverse fields.

Deviations are expected when polarization is lost through slow formation of the radical. It is seen that the whole frequency spectrum collapses to two lines in high fields. This is independent of the number of nuclei coupling with the unpaired electron. At ≈ 20 G the off-diagonal elements in the secular determinant in basis $|\chi_i\rangle$ (4.3) are of the same order of magnitude as the Zeeman terms, and the spectrum is most complex.

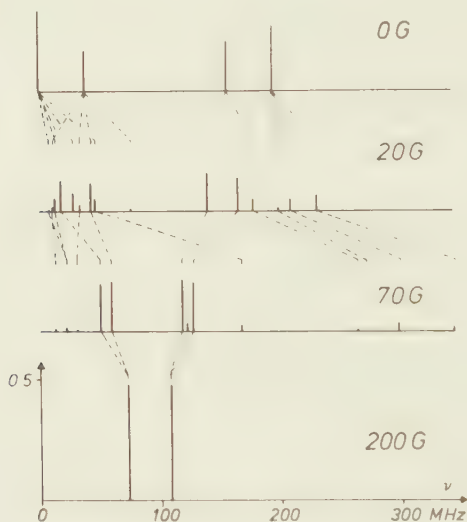


Fig.4.3: Calculated μ SR spectra for a μ -e-p-system in different transverse fields.
hfccs: $A_p = 56$ MHz, $A_\mu = 3.18 \cdot 56$ MHz.

It is predicted to be much simpler in zero field with only three non-zero frequency transitions in our example. However, it has to be pointed out that in the absence of an external field there is no directive force which determines the direction of the muon precession. For this reason the observable muon polarization oscillates back and forth

in the x-direction, whereas no polarization should be observed in a telescope perpendicular to the initial muon polarization, i.e. in the y-z-plane. This can be seen in figs. (4.4a,b). Here, muon precession frequencies are plotted as a function of the transverse magnetic field for a muon-electron and a muon-electron-proton system. (Precession of the bare muon defines the positive direction.) In zero field, the situation is symmetric, i.e. for each transition of positive frequency, there exists one of negative frequency with the same amplitude. Hence, the y and z-components of polarization are cancelled by the respective components of opposite sense of precession.

The high field side of fig.4.4b is identical to fig.4.4a. Here the situation is governed solely by the muon-electron coupling. Note that one frequency goes through zero at $B = 36.72 \cdot |A_\mu|$ Gauss (A_μ in MHz) due to level crossing. Greatly above this point, in the Paschen-Back region, the two radical frequencies are displaced symmetrically by $\frac{1}{2} A_\mu$ about the signal of the bare muon. Around 150 G the influence of the additional proton (fig.4b) causes splitting of the two radical frequencies. Below 100 G those transitions forbidden in high field appear with low intensities (broken lines). Some of them grow to considerable intensities at ≈ 20 G (compare fig.4.3).

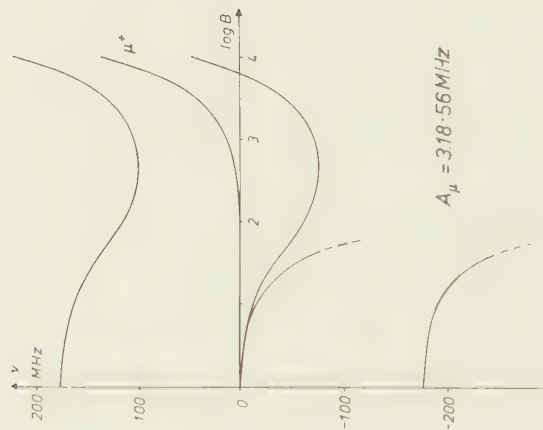


Fig.4.4a: Field dependence of transverse field μ SR frequencies for the free μ^+ and a μ -e-system. Broken lines indicate low intensity.

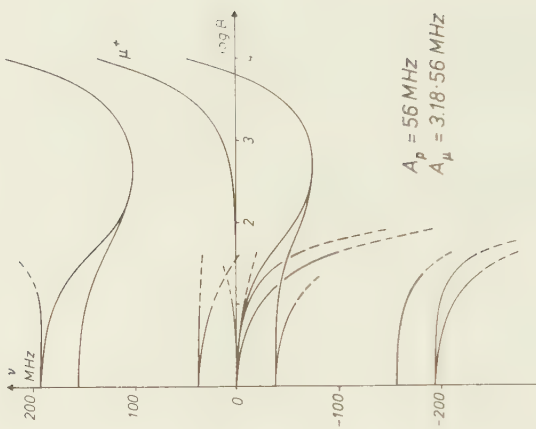


Fig.4.4b: Field dependence of transverse field μ SR frequencies for the free μ^+ and a μ -e-p- system. Broken lines indicate low intensity.

4.1.6. Perturbation Treatment

In high fields the eigenvalues to $\hat{H}$ (4.1) approach the eigenvalues to $\hat{H}_z$ (4.4)

$$E_n = v_e m^s - v_\mu m^\mu - \sum_k v_k m^k + A_\mu m^s m^\mu + \sum_k A_k m^s m^k. \quad (4.31)$$

Using selection rule (4.24) we immediately obtain the two transition frequencies

$$v_{mn} = v_\mu \pm \frac{1}{2} A_\mu, \quad (4.32)$$

which are the same ones as those encountered in ENDOR experiments of single spin- $\frac{1}{2}$ nuclei [60]. Considerable deviations from (4.32) are to be seen in both experimental and numerical results for those fields where most experiments have been performed. A more rigorous approach of analysis than using (4.32) must be sought.

In μ SR one looks at a transition of the muon which is coupled directly to the unpaired electron but only indirectly to other nuclei. To apply perturbation theory we may therefore start with the complete muon-electron Hamiltonian

$$\hat{H}^0 = v_e \hat{S}_z - v_\mu \hat{I}_z^\mu + A_\mu \hat{S} \cdot \hat{I}^\mu. \quad (4.33)$$

As an example we introduce a set of N equivalent nuclei as the perturbation

$$\begin{aligned} \hat{H}' &= - \sum_k^N v_k \hat{I}_z^k + \sum_k^N A_k \hat{S} \cdot \hat{I}^k \\ &= -v_k \hat{K}_z + A_k \hat{S} \cdot \hat{K}. \end{aligned} \quad (4.34)$$

This is a good approximation at least for $A_k \leq A_\mu$. We use K as the quantum number for the total nuclear angular momentum $K = \sum_k \hat{I}^k$, and M_k for its z-component $\hat{K}_z$. K can take the values $K_{\text{Max}}, K_{\text{Max}}-1, K_{\text{Max}}-2, \dots, 0$ (or $\frac{1}{2}$) with different statistical probabilities. The eigenkets to $\hat{H}^0$ are products of muonium analogous eigenfunctions (see

Table 4.1

Zero order eigenvectors, eigenvalues^{a)} and transition frequencies

$ 1, K, M_K\rangle = e\rangle \otimes e\rangle \otimes K, M_K\rangle$	$E_1^0 = \frac{1}{4}A_{\mu} + \frac{1}{2}(\nu_e - \nu_{\mu})$
$ 2, K, M_K\rangle = s \alpha^{\mu}\rangle \beta^e\rangle K, M_K\rangle + c \beta^{\mu}\rangle \alpha^e\rangle K, M_K\rangle$	$E_2^0 = -\frac{1}{4}A_{\mu} + \frac{1}{2}[A_{\mu}^2 + (\nu_e + \nu_{\mu})^2]^{\frac{1}{2}}$
$ 3, K, M_K\rangle = e\rangle \otimes e\rangle \otimes K, M_K\rangle$	$E_3^0 = \frac{1}{4}A_{\mu} - \frac{1}{2}(\nu_e - \nu_{\mu})$
$ 4, K, M_K\rangle = -s \beta^{\mu}\rangle \alpha^e\rangle K, M_K\rangle + c \alpha^{\mu}\rangle \beta^e\rangle K, M_K\rangle$	$E_4^0 = -\frac{1}{4}A_{\mu} - \frac{1}{2}[A_{\mu}^2 + (\nu_e + \nu_{\mu})^2]^{\frac{1}{2}}$
$\nu_{1c}^0 = \nu_{-} - \Omega^c$	$A_{1c} \sim c^2$
$\nu_{23}^0 = \nu_{-} + \Omega$	$A_{23} \sim s^2$
$\nu_{14}^0 = A_{+} + \nu_{-} + \Omega$	$A_{14} \sim s^2$
$\nu_{43}^0 = -A_{+} + \nu_{-} - \Omega$	$A_{43} \sim c^2$

a) frequency units

$$b) \quad c = (1/\sqrt{2}) \{1 + (\nu_e + \nu_{\mu})/[A_{\mu}^2 + (\nu_e + \nu_{\mu})^2]^{\frac{1}{2}}\}^{\frac{1}{2}}$$

$$s = (1/\sqrt{2}) \{1 - (\nu_e + \nu_{\mu})/[A_{\mu}^2 + (\nu_e + \nu_{\mu})^2]^{\frac{1}{2}}\}^{\frac{1}{2}}$$

$$c) \quad \nu_{ij} = E_i - E_j$$

$$\nu_{-} = \frac{1}{2}(\nu_e - \nu_{\mu})$$

$$\Omega = \frac{1}{2} \{[(\nu_e + \nu_{\mu})^2 + A_{+}^2]^{\frac{1}{2}} - A_{+}\}$$

for example [55]) and a nuclear wavefunction $|K, M_K\rangle$. They are given in table 4.1 together with zero order energies E_i^0 , transition frequencies ν_{mn}^0 and their relative amplitudes A_{mn} . The mixing coefficient s decreases rapidly with increasing field, so that in moderate and high fields only ν_{12}^0 and ν_{43}^0 are of significant intensity.

The first order corrections to the energies

$$E_n^1 = \langle n | \hat{H}' | n \rangle \quad (4.35)$$

are given in table 4.2, as are the two important transition frequencies. The two μ SR lines are split into symmetric multiplet patterns characteristic of magnetic resonance. The splitting increases with decreasing field because of its proportionality to s^2 , and for a given field it grows with increasing A_K .

Table 4.2

First order energy corrections and transition frequencies

E_{1,K,M_K}^1	$= -M_K \nu_K + \frac{1}{2} A_K M_K$
E_{2,K,M_K}^1	$= -M_K \nu_K + \frac{1}{2} A_K M_K (c^2 - s^2)$
E_{3,K,M_K}^1	$= -M_K \nu_K - \frac{1}{2} A_K M_K$
E_{4,K,M_K}^1	$= -M_K \nu_K - \frac{1}{2} A_K M_K (c^2 - s^2)$
$\nu_{12}^1(M_K)$	$= \nu_{12}^0 + A_K M_K s^2$
$\nu_{43}^1(M_K)$	$= \nu_{43}^0 + A_K M_K s^2$

The second order corrections to the energies are

$$E_n^{(2)} = - \sum_{m \neq n} \frac{|\langle m | \hat{H}' | n \rangle|^2}{E_m^{(0)} - E_n^{(0)}} . \quad (4.36)$$

Here, the effective part of $\hat{H}'$ takes the form $\frac{1}{2}A_K(\hat{S}_+\hat{R}_- + \hat{S}_-\hat{R}_+)$, which yields the results collected in table 4.3. The relative importance of the second order term may be demonstrated with our example of the electron-muon-proton system (compare figs. 4.3, 4.4b). We calculate the splitting of the lines at 200 G to be 1.29 MHz in first order with an additional 0.41 MHz in second order. Thus we have 1.70 MHz from perturbation theory compared to 1.65 MHz in the full calculation. Such splittings can still be resolved. A typical resolution in μ SR experiments is 0.3 MHz.

The important result is that the hfcc A_μ can still be determined directly from two frequencies, which belong to the same M_K :

$$|A_\mu| = |\nu_{12}^{(1)}(M_K)| \pm |\nu_{43}^{(1)}(M_K)| . \quad (4.37)$$

The "+" applies to the case of high enough fields where both frequencies have the same sign, i.e. for $B > 36.72 \cdot A_\mu$ (compare fig.4.4). The second order corrections are not symmetric with respect to the zero order frequencies. They disturb the first order multiplet pattern considerably and make a determination of A_μ more difficult.

It should be noted that only the magnitude $|A_\mu|$ can be determined from first order μ SR spectra. In principle $|A_K|$ can also be obtained from the line splitting, although this method is not very accurate. Note that the second order contribution to the splitting is sensitive to the sign of A_μ .

Table 4.3

Second order energy corrections and transition frequencies^{a)}.

E_{1,K,M_K}^2	$= -\frac{1}{4} A_K^2 [K(K+1) - M_K(M_K+1)] \left[\frac{C^2}{E_4^0 - E_1^0} + \frac{S^2}{E_2^0 - E_1^0} \right]$
E_{2,K,M_K}^2	$= -\frac{1}{4} A_K^2 \left\{ [K(K+1) - M_K(M_K+1)] \frac{C^2}{E_3^0 - E_2^0} + [K(K+1) - M_K(M_K-1)] \frac{S^2}{E_1^0 - E_2^0} \right\}$
E_{3,K,M_K}^2	$= -\frac{1}{4} A_K^2 [K(K+1) - M_K(M_K-1)] \left[\frac{C^2}{E_2^0 - E_3^0} + \frac{S^2}{E_4^0 - E_3^0} \right]$
E_{4,K,M_K}^2	$= -\frac{1}{4} A_K^2 \left\{ [K(K+1) - M_K(M_K-1)] \frac{C^2}{E_1^0 - E_4^0} + [K(K+1) - M_K(M_K+1)] \frac{S^2}{E_3^0 - E_4^0} \right\}$
$\nu_{12}^2(K, M_K)$	$= \nu_{12}^0 + A_K M_K S^2 - \frac{1}{4} A_K^2 \left\{ [K(K+1) - M_K(M_K+1)] \cdot \frac{C^2}{\nu_{14}^0 \cdot \nu_{23}^0} - [K(K+1) - M_K^2] \cdot \frac{2S^2}{\nu_{12}^0} \right\}$
$\nu_{43}^2(K, M_K)$	$= \nu_{43}^0 + A_K M_K S^2 + \frac{1}{4} A_K^2 \left\{ [K(K+1) - M_K(M_K-1)] \cdot \frac{C^2}{\nu_{14}^0 \cdot \nu_{23}^0} + [K(K+1) - M_K^2] \cdot \frac{2S^2}{\nu_{43}^0} \right\}$

a) Not valid near the crossing of E_1^0 and E_2^0

4.1.7. Analytical Solution for Zero Field

μ SR spectra are considerably simplified in the absence of a magnetic field (fig. 4.3) as compared to intermediate fields. This is particularly so in the presence of equivalent nuclei. Thus it may be possible to observe muonic radical spectra in zero field.

We confine ourselves to the case of a radical with N equivalent nuclei coupled to the unpaired electron, in addition to the muon. The Hamiltonian is

$$\begin{aligned}\hat{H} &= A_{\mu} \hat{S} \cdot \hat{I}^{\mu} + \sum_k^N A_k \hat{S} \cdot \hat{I}^k \\ &= A_{\mu} \hat{S} \cdot \hat{I}^{\mu} + A_k \hat{S} \cdot \hat{K},\end{aligned}\quad (4.38)$$

using the notation introduced in (4.34). The Slater determinant factorizes into subdeterminants according to M_F . An example of a subdeterminant is given in table 4.4. It is written in the basis of the product spin functions

$$|\chi_i\rangle = |\chi_i^{\mu}\rangle |\chi_i^e\rangle |\chi_i^k\rangle, \quad (4.39)$$

which are characterized by the quantum numbers for the z-components of the spins, m^{μ} , m^s and M. The general solutions for the energies (table 4.5) are independent of M. They have been found already by Meier and Schenck [71]. Calculation of the expansion coefficients is lengthy but straightforward. The solutions are given in table 4.5. Note that for E_1 and E_3 they are independent of the two hfcc's and are similar to the Clebsch-Gordan coefficients for two coupled spins ($\vec{J} = \vec{S} + \vec{I}$, $S = 1$).

For E_2 and E_4 the coefficients, and hence the intensities of μ SR transitions, depend on A_{μ}/A_k . Beck et al. [63] calculate simple expressions for μ SR intensities in U_2 -centers, using an approximate Hamiltonian which is valid for $A_{\mu} \gg A_k$. This approximation does not usually hold for muonic radicals, where it is better to use the exact coefficients.

Table 4.4

General Slater subdeterminant for the Hamiltonian (4.38)

$$\begin{array}{c}
 \begin{array}{cccc}
 \chi_1 & \chi_2 & \chi_3 & \chi_4 \\
 \begin{bmatrix} \frac{1}{4} A_{\mu} + \frac{1}{2} M \cdot A_k - E \\ 0 \\ \frac{1}{2} [K(K+1) - M(M+1)]^{1/2} A_k \\ 0 \end{bmatrix} & \begin{bmatrix} 0 \\ -\frac{1}{4} A_{\mu} + \frac{1}{2} (M+1) \cdot A_k - E \\ \frac{1}{2} A_{\mu} \\ \frac{1}{2} [K(K+1) - (M+1)(M+2)]^{1/2} A_k \end{bmatrix} & \begin{bmatrix} \frac{1}{2} [K(K+1) - M(M+1)]^{1/2} A_k \\ \frac{1}{2} A_{\mu} \\ -\frac{1}{4} A_{\mu} - \frac{1}{2} (M+1) \cdot A_k - E \\ 0 \end{bmatrix} & \begin{bmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{4} A_{\mu} - \frac{1}{2} (M+2) A_k - E \end{bmatrix} \\
 \chi_2 & \chi_3 & \chi_4 \\
 \begin{bmatrix} 0 \\ -\frac{1}{4} A_{\mu} + \frac{1}{2} (M+1) \cdot A_k - E \\ \frac{1}{2} A_{\mu} \\ \frac{1}{2} [K(K+1) - (M+1)(M+2)]^{1/2} A_k \end{bmatrix} & \begin{bmatrix} \frac{1}{2} [K(K+1) - M(M+1)]^{1/2} A_k \\ \frac{1}{2} A_{\mu} \\ -\frac{1}{4} A_{\mu} - \frac{1}{2} (M+1) \cdot A_k - E \\ 0 \end{bmatrix} & \begin{bmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{4} A_{\mu} - \frac{1}{2} (M+2) A_k - E \end{bmatrix} \\
 \chi_3 & \chi_4 \\
 \begin{bmatrix} \frac{1}{2} [K(K+1) - M(M+1)]^{1/2} A_k \\ \frac{1}{2} A_{\mu} \\ -\frac{1}{4} A_{\mu} - \frac{1}{2} (M+1) \cdot A_k - E \\ 0 \end{bmatrix} & \begin{bmatrix} \frac{1}{2} [K(K+1) - (M+1)(M+2)]^{1/2} A_k \\ 0 \\ 0 \\ \frac{1}{4} A_{\mu} - \frac{1}{2} (M+2) A_k - E \end{bmatrix} \\
 \chi_4 \\
 \begin{bmatrix} 0 \\ \frac{1}{2} [K(K+1) - (M+1)(M+2)]^{1/2} A_k \\ 0 \\ \frac{1}{4} A_{\mu} - \frac{1}{2} (M+2) A_k - E \end{bmatrix}
 \end{array}
 \end{array}
 = 0$$

$$\mu \quad e \quad k$$

$$|\chi_1\rangle = \left| \frac{1}{2}, \frac{1}{2}, M \right\rangle$$

$$|\chi_2\rangle = \left| -\frac{1}{2}, \frac{1}{2}, M+1 \right\rangle$$

$$|\chi_3\rangle = \left| \frac{1}{2}, -\frac{1}{2}, M+1 \right\rangle$$

$$|\chi_4\rangle = \left| -\frac{1}{2}, -\frac{1}{2}, M+2 \right\rangle$$

$$K = K_{\text{Max}}, K_{\text{Max}}^{-1}, K_{\text{Max}}^{-2}, \dots, 0 \text{ (or } \frac{1}{2} \text{)}.$$

$$M = K, K-1, K-2, \dots, -K+1, -K, -K-1, -K-2.$$

Table 4.

Energies and expansion coefficients for 3-spin system in zero field for $I \geq 1$

$n >$	E_n	C_1	C_2	C_3	C_4
1	$\frac{1}{2}A_{\mu} + \frac{1}{2}K \cdot A_K$	$\left[\frac{(K+M-1)(K+M+2)}{2(2K+1)(K+1)} \right]^{1/2}$	$\left[\frac{(K+M+2)(K-M)}{2(2K+1)(K+1)} \right]^{1/2}$	$C_3 = C_2$	$\left[\frac{(K-M)(K-M-1)}{2(2K+1)(K+1)} \right]^{1/2}$
2	$-\frac{1}{2}(A_{\mu} + A_K) + \frac{1}{2}A_K \cdot W$	$\frac{1}{2} \left[\frac{(K+M+1)(K-M)}{W(W-B)} \right]^{1/2}$	$\frac{B-W-M-1}{2[W(W-B)]^{1/2}}$	$\frac{-B+W-M-1}{2[W(W-B)]^{1/2}}$	$-\frac{1}{2} \left[\frac{(K-M-1)(K+M+2)}{W(W-B)} \right]^{1/2}$
3	$\frac{1}{4}A_{\mu} - \frac{1}{2}(K+1) \cdot A_K$	$\left[\frac{(K-M)(K-M-1)}{2K(2K+1)} \right]^{1/2}$	$-\left[\frac{(K+M+1)(K-M-1)}{2K(2K+1)} \right]^{1/2}$	$C_3 = C_2$	$\left[\frac{(K+M+2)(K+M+1)}{2K(2K+1)} \right]^{1/2}$
4	$-\frac{1}{4}(A_{\mu} + A_K) - \frac{1}{2}A_K \cdot W$	$\frac{1}{2} \left[\frac{(K+M+1)(K-M)}{W(W+B)} \right]^{1/2}$	$\frac{B+W-M-1}{2[W(W+B)]^{1/2}}$	$\frac{-B-W-M-1}{2[W(W+B)]^{1/2}}$	$-\frac{1}{2} \left[\frac{(K-M-1)(K+M+2)}{W(W+B)} \right]^{1/2}$

$$a) \quad |n\rangle = \sum_{i=1}^n c_i |i\rangle$$

abbreviations: $W = [B^2 + K(K+1)]^{1/2}$

$$B = \frac{A_{\mu}}{A_K} - \frac{1}{K}$$

A numerical example will illustrate the situation. The radical $(\text{CH}_3)_2\dot{\text{C}}\text{C}(\text{CH}_3)_2\text{Mu}$ is formed by addition of Mu to tetramethylethylene. We have determined A_μ to be 161 MHz (section 4.2) and use $A_k = 64$ MHz from ESR measurements [72]. The six β -protons are equivalent, and can combine to the following angular momenta (with their relative statistical probabilities g in parentheses): $K=3(1), 2(5), 1(9), 0(5)$. Fig.(4.5a) displays the energy levels, characterized by the total angular momentum F , and the allowed μSR transitions $\Delta F = 0, \pm 1(4.23)$ and $\Delta K = 0$ ($\hat{H}$ does not mix states with different K and the transition operator acts only on the muon wavefunction). For $K = 0$ the situation is akin to Mu, therefore there are only two states, $F = 0, 1$. Fig.(4.5b) gives the Fourier spectrum, calculated based on (4.14) and using the expansion coefficients obtained from table 4.5. The intensities are weighted with the statistical probability (proportional to g) for a state K to occur. We see that even for the state $K = 3$ which has the lowest probability (5%) there are transitions of considerable intensity. The total intensity (normalized to unity; note that 27% of the polarization does not oscillate) is distributed among 16 transitions. Two lines coincide by chance at 102 MHz and two at 161 MHz. The simplicity of the spectrum comes from the equivalence of the 6 protons. If they were inequivalent the spectrum would consist of 1688 lines (4.30).

The energy levels depend on the signs of the coupling constants (table 4.5). It is therefore clear that the relative signs are obtained from the zero field spectrum (not so from the high field spectrum). This has been recognized before for magnetic resonance [73].

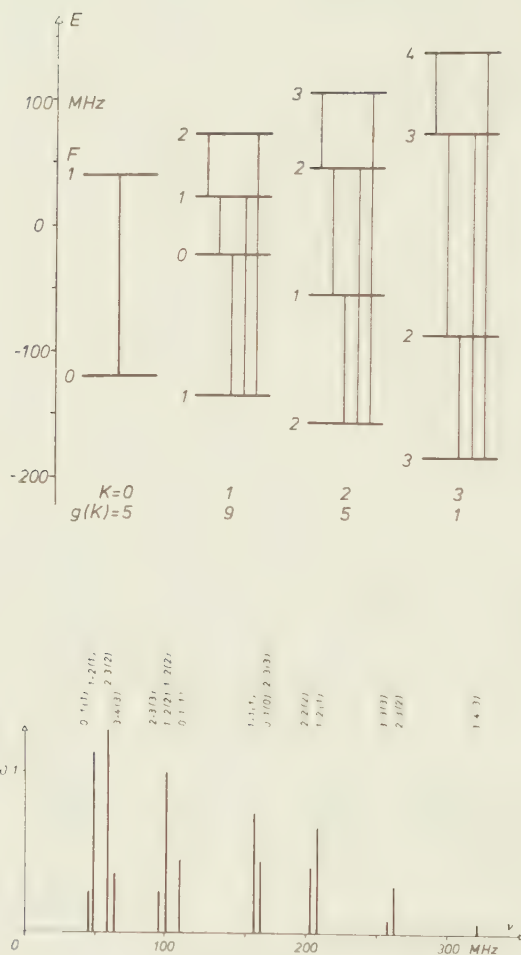


Fig.4.5: $(\text{CH}_3)_2\dot{\text{C}}\text{C}(\text{CH}_3)_2\text{Mu}$ in zero external field.
 $A_\mu = 161 \text{ MHz}$, $A_p = 64 \text{ MHz}$.

- energy levels and allowed transitions
- calculated Fourier amplitudes for the transitions $F-F'(K)$ assuming full polarization in the radical.

4.2. Experimental Results

The radicals observed are listed and compared with their hydrogen analogues in table 4.6. The structures proposed are based on the principle that the thermodynamically more stable radicals are formed, in analogy to the chemistry of H. It is known that addition of thermal hydrogen isotopes to terminal olefins occurs almost exclusively (>95%) at the CH_2 group [74]. Addition does not occur at the central carbon atoms of 1,3 - butadiene [74]. Thus it seems reasonable that two muonic allyl radicals are formed in both isoprene (fig.4.6) and 1,3 - pentadiene. Furthermore muonic t-butyl radical is formed from isobutene.

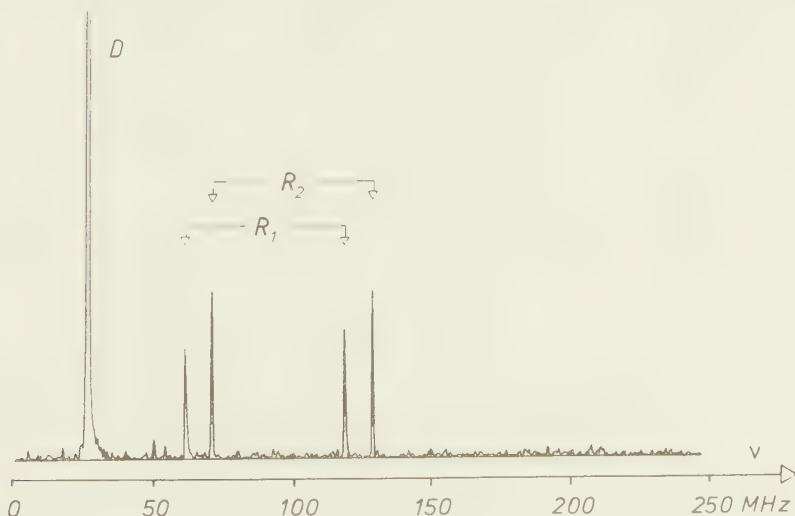


Fig.4.6: Muon precession frequencies obtained with isoprene at 2 kG. D: muons in diamagnetic environments, R_1 and R_2 : muonic radicals.

Table 4.5

Hyperfine Coupling Constants of Muonic Radicals at Ambient Temperature and Comparison with Hydrogen Analogues.

substrate	radical	$A_{\mu} \cdot \mu / \mu$ [MHz]	A_P [MHz] ^{a)}	$A_{\mu} \cdot \mu / A_P \cdot \mu$
isobutene	$(CH_3)_2\dot{C}CH_2Mu$	91.7	63.7 (203)	1.44
tetramethylethylene	$(CH_3)_2CC(CH_3)_2Mu$	50.67	30.18 (298)	1.68
acetone	$CH_3\dot{C}COMu$	91.2	0.9 (300)	9.1
isoprene	$\left\{ \begin{array}{l} CH_2 = C(CH_3)CHCH_2Mu \\ CH_2Mu\dot{C}(CH_3)CH = CH_2 \end{array} \right.$	56.8 or 62.7 62.7 or 56.8	37.8 (300) 42.91 (363)	1.50 - 1.66 1.32 - 1.46
1,3-pentadiene	$\left\{ \begin{array}{l} CH_2 = CHCHCHMuCH_3 \\ CH_2MuCHCH = CHCH_3 \end{array} \right.$	53.1 or 57.4 57.4 or 53.1	39.74 (140)	1.34 - 1.44
benzene	cyclohexadienyl	161.6	133.7 (288)	1.21
benzene- d_6	cyclohexadienyl- d_6	161.4	133.9 (114)	1.20
toluene	$\left\{ \begin{array}{l} o\text{-methyl cyclohexadienyl} \\ p\text{-methyl cyclohexadienyl} \end{array} \right.$	154.1 or 160.4 160.4 or 154.1	123.9 (300)	1.24 - 1.29
thiophene	2-thiophenyl	106.5	95.3 (130)	1.12

a) values taken from Fischer and Hellwege [79]; temperature [K] in parentheses

H adds to the oxygen of acetone [36], and Mu is expected to do the same. Only one radical is formed in tetramethylethylene. The field dependence of the frequencies (fig.4.7, table 4.7) is as expected (table 4.1).

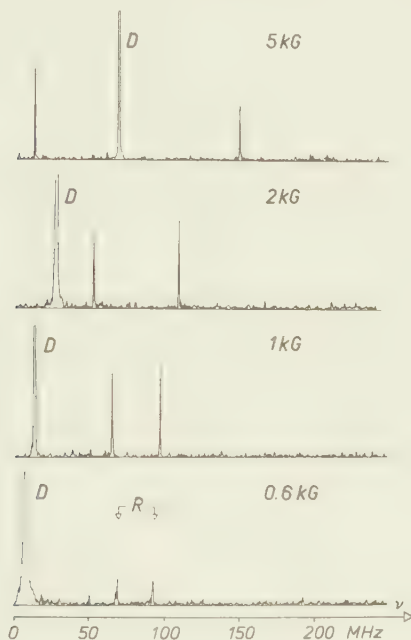


Fig.4.7: Muon precession frequencies obtained with tetramethylethylene at various magnetic fields and ambient temperature.
D: muons in diamagnetic environment,
R: muonic radicals.

H is known to add to benzene to form the cyclohexadienyl radical [75]. μ SR spectra of its muonic analogue are displayed in fig. 4.8. Each line is split by 1.5 MHz at 1 kG.

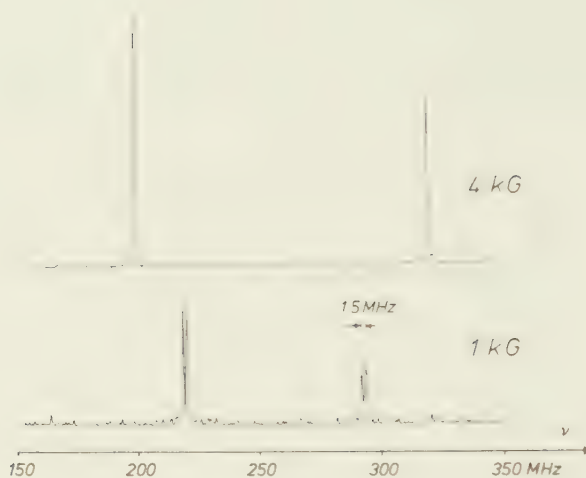


Fig.4.8: μ SR frequency spectra obtained with benzene at ambient temperature. Only the radical signals are displayed.

Table 4.7

Precession frequencies in tetramethylethylene at ambient temperature (± 0.2 MHz)

B [kG]	ν_{μ} [MHz]	$ \nu_{12} $ [MHz]	$ \nu_{43} $ [MHz]	$ \nu_{12} - \nu_{43} $ a) [MHz]
0.3	3.9	70.7	90.6	161.3
0.6	8.1	68.9	92.7	161.6
1.0	13.5	64.6	96.3	160.9
2.0	27.2	52.2	108.8	161.0
3.0	40.7	39.0	121.8	160.8
4.0	54.1	25.7	135.2	160.9
5.0	67.8	12.3	148.6	160.9

a) ν_{12} and ν_{43} are assumed to have opposite signs, in accord with theoretical predictions.

DiGregorio et al. [76] and Bennett and Mile [74] find that H adds to toluene in the ortho position. This is in contradiction to Devolder and Goudmand [77] who believe to see only the product of meta addition. We observe two muonic radicals in toluene and assign them tentatively to the ortho and para addition products since these two positions usually show similar chemical behaviour. As is seen in the μ SR spectrum obtained with toluene (fig.4.9) there appears a further frequency at 200.8 MHz (marked with an asterisk in fig.4.9). This may belong to a third radical, but there is no significant peak corresponding to the second frequency.

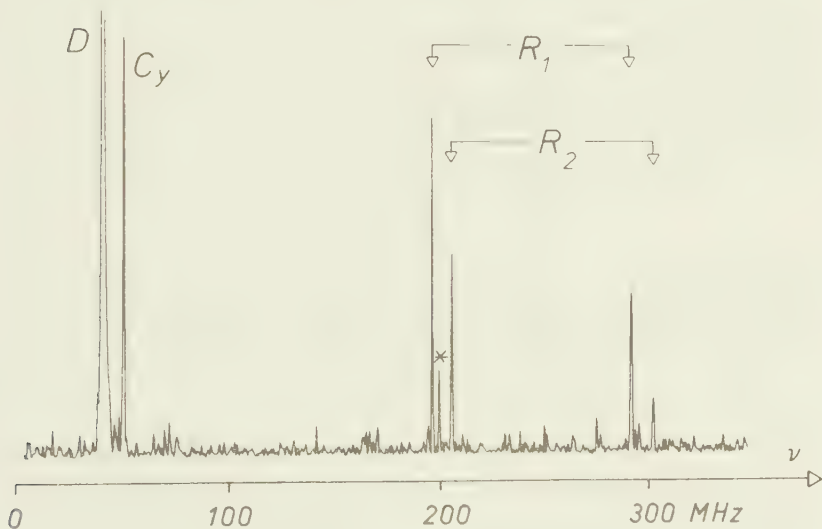


Fig.4.9: Muon precession frequencies obtained with toluene at 3kG and ambient temperature. D: muons in diamagnetic environments, Cy: cyclotron frequency, R_1, R_2 : muonic radicals. The asterisk marks a frequency which may belong to a further radical.

H adds to thiophene to form the 2-thiophenyl radical [78].

In table 4.6 the hfccs of muonic radicals are compared with those of the hydrogen atom analogues. In the absence of isotope effects the muon and proton hfcc's should be given by the ratio of their magnetic moments, $\mu_p/\mu_\mu = 0.3141$. The discrepancies between columns 3 and 4 of table 4.6 clearly demonstrate the existence of isotope effects. In all cases the muon coupling constant is larger than predicted from the relative magnetic moments.

Due to the nature of radical addition, the hfccs are of the "β" type, i.e. the muonium atom is bound to an atom adjacent to the radical centre (or conjugated system). Such constants are usually quite temperature dependent [60]. This behaviour has been measured for the Mu adducts of isoprene [80] and tetramethylethylene [81], and is reported in table 4.8 and fig. 4.10. The equilibrium conformations (fig. 4.10) are discussed in section 4.3.2.

Table 4.8

Temperature dependence of A_μ for muonic radicals formed in tetramethylethylene and in μ -isobutene.

tetramethylethylene		isobutene	
T[K]	A_μ [MHz] ^{a)}	T[K]	A_μ [MHz] ^{b)}
292	161.15	295	292.0
245	159.61	275	296.9
230	159.06	247	305.5
223	158.65	215	320.3
219	158.36	190	335.4
211	157.81	156	356.0
207	157.58	134	372.0
194	156.87		

a) accurate to ± 0.15 MHz

b) accurate to ± 0.3 MHz

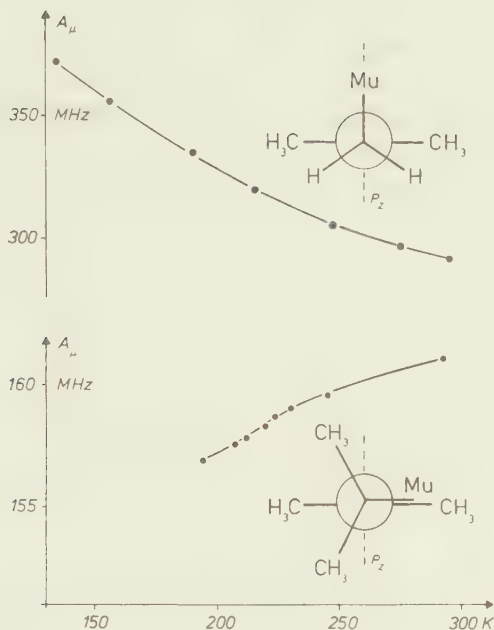


Fig.4.10: Temperature dependence of A_μ in radicals formed by addition of Mu to isobutene (top) and tetramethylethylene (bottom), together with the proposed equilibrium conformations. Note the different scales for A_μ .

No radicals have been found in the following unsaturated substances: cyclohexene at room-temperature and at 173 K, and acetonitrile and hexafluorobenzene at room-temperature.

From the considerations in section 4.1 it is clear that radicals are to be observed most easily in high fields (first report ref.[82]). However, one may hope that for particularly simple radicals (few or equivalent spins) it is possible to get reasonable spectra also in intermediate

or in zero field. In intermediate fields where banding of frequencies may occur evidence for observation of radicals has been reported by Bucci et al.[83]. Recently we were successful in zero field (with the earth magnetic field compensated to ≤ 0.2 G). Fig.4.11 shows the Fourier power spectrum for the radical $(\text{CH}_3)_2\dot{\text{C}}\text{C}(\text{CH}_3)_2\text{Mu}$ that was predicted to be particularly simple (section 4.1.7, fig. 4.5). It was obtained with a high statistics run ($3.7 \cdot 10^7$ events) in a positron counter telescope in the direction of the muon polarization in the beam.

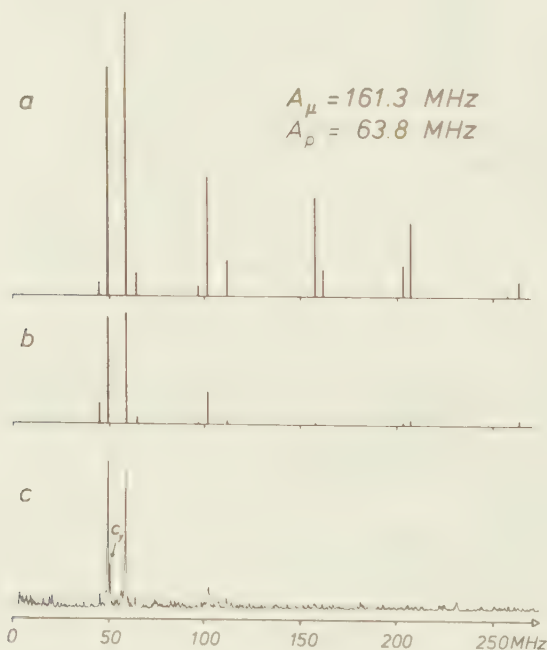


Fig.4.11: Muon oscillation frequencies for the radical $(\text{CH}_3)_2\dot{\text{C}}\text{C}(\text{CH}_3)_2\text{Mu}$ in the absence of an external field.

- a) calculated Fourier power spectrum for full transfer of polarization from Mu to the radical (Mu addition rate $\geq 10^{11} \text{ s}^{-1}$)
- b) calculated spectrum for partial transfer of polarization (Mu addition rate $\approx 10^{10} \text{ s}^{-1}$)
- c) experimental spectrum with counters in the direction of the initial muon polarization, Cy: cyclotron frequency.

In agreement with prediction there was no signal in a perpendicular telescope except for a background peak at 50.7 MHz corresponding to the cyclotron frequency. Three frequencies are clearly present, three more exceed the noise level only slightly. The asymmetry in each of the two intense peaks is about 0.5%. The frequencies that are predicted above 150 MHz (4.11a) are not observed. To check whether this effect could be due to incomplete transfer of polarization we calculated the spectrum using equation (4.16, $\lambda_2=0$) in place of (4.14, 4.15). The observable polarization on a radical frequency ω_{nm}^R corresponds to the real part in (4.16), i.e. it is a sum of contributions from the four frequencies ω_{jl}^{Mu} , each term in the sum being proportional to

$$\frac{\lambda_1^2}{\lambda_1^2 + (\omega_{mn}^R - \omega_{jl}^{Mu})^2} \quad (4.40)$$

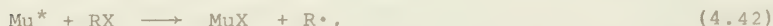
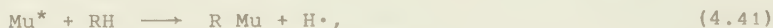
and to a collection of matrix elements W_{1jmn} (4.17). This means that the rate of formation of the radical, λ_1 , has to compete with the difference in the frequencies between the muon oscillation in Mu and in the radical. For $\lambda_1 \approx 10^{10} \text{ s}^{-1}$ it is reasonable to approximate (4.40) by unity for $\omega_{jl}^{Mu} = 0$, and by 0 for $\omega_{jl}^{Mu} = 2.80 \cdot 10^{10} \text{ rad s}^{-1}$. The resulting spectrum as given in fig.4.11b (same scale as a) is in striking agreement with the experimental one.

Further the spectrum proves the structure of the radical that was based on the assumption that Mu adds as a thermal hydrogen isotope. The radical has to have six equivalent protons but no further nuclei coupling. The hffcs agree well with the high field values (section 4.1.7). Also they are of the same sign. This is no surprise since they belong both to β -couplings.

4.3. Discussion

4.3.1. Radical Formation

In all liquids so far investigated by means of μ SR there is a substantial fraction of muon polarization P_D precessing at the frequency of the free muon. An earlier assumption was [55, 66] that it stems from reactions of epithermal Mu^* of types



in analogy to the well known hot reactions of its heavier isotope T^* [84]. However, there is recent evidence [11] that hot reactions of Mu^* play at most a minor role, at least in aqueous solutions. The problem has not yet been investigated for non-aqueous systems. In unsaturated compounds P_D may well arise via addition of thermal Mu (reaction 1.2) followed by decomposition, e.g.



Thermal H atom addition is sufficiently exothermic that decomposition can occur, for T^* even in the liquid state [85], although some of the radicals are stabilized by intermolecular collisions.

So far there is no need to postulate hot reactions for the formation of muonic radicals, since these can all be explained in terms of thermal Mu addition. Hot reactions are expected to be almost non-selective. Accordingly two radicals should be produced from isobutene, acetone and thiophene, and four from isoprene, 1,3-pentadiene and toluene. This is in contradiction to our observation. Addition of hot Mu ought to be fast enough to conserve muon polarization, whereas sufficiently slow (and thus necessarily thermal) addition would result in a frequency dependent loss of polarization [68]. Preliminary experiments show that the relative polarization at the two high field radical

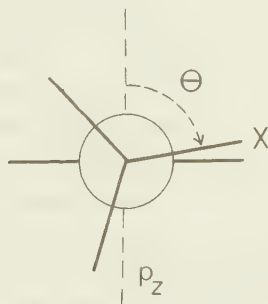
frequencies in tetramethylethylene is temperature dependent in the expected way [86]. Further the sum of observable polarization in radicals and diamagnetic compounds is less than unity in all the unsaturated compounds investigated, i.e. there is a missing fraction of polarization. Fig. 4.11 is of particular importance to this question. The zero field spectrum of $(\text{CH}_3)_2\dot{\text{C}}\text{C}(\text{CH}_3)_2\text{Mu}$ clearly disagrees with what one would expect for addition of hot Mu to the olefin. The spectrum agrees with what one expects for a rate of addition of $\approx 10^{10}\text{s}^{-1}$. This can be less by one order of magnitude but certainly not much more.

4.3.2. Hyperfine Coupling Constants

As mentioned above the muon is bound at the β -position in muonic radicals. Corresponding hfccs are described by

$$\langle A \rangle = B + A_0 \langle \cos^2 \theta \rangle \quad (4.44)$$

[87], where the first term, B , represents a contribution arising from spin polarization and the second term describes the angular dependence of the spin density at the β -nucleus. The definition of θ is given in a Newman projection [88]:



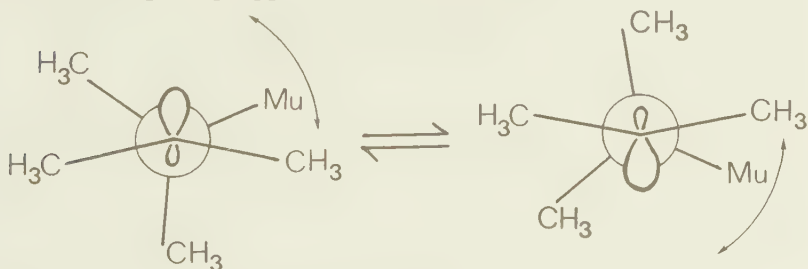
where the projection is in the direction of the axis of internal rotation. The observed coupling constant is a

weighted average over conformations with different θ . The weighting depends on the potential barrier to internal rotation, on the reduced moment of inertia, and on the temperature. In the high temperature limit there is essentially free rotation with equal probability for all θ . Here, A becomes equal to $B + \frac{1}{2}A_0$. A will increase with decreasing temperature for an equilibrium conformation $-45^\circ < \theta_0 < 45^\circ$ and decrease for $45^\circ < \theta_0 < 135^\circ$ (see refs. [72, 89] for extensive theoretical and experimental studies).

The hfcc for the nine equivalent protons in the t-butyl radical is practically temperature independent [90] because of the C_3 symmetry in the methyl groups (This value corresponds to that for free rotation). The strong negative temperature dependence for A_μ in the analogous muonic radical (table 4.8, fig.4.10) indicates an equilibrium conformation with $\theta_0=0$, i.e. Mu rather than H is eclipsed by the half-filled p_z orbital. This would be so if Mu is bulkier than H, so that larger steric hindrance occurs if the lighter isotope eclipses a methyl group. We estimate the difference in the effective radii ($\hat{=}$ van der Waals radii) of Mu and H from the difference in the zero point vibrational amplitudes.

In the harmonic approximation $\langle (X-X_0)^2 \rangle_{\text{Mu}}^{1/2} - \langle (X-X_0)^2 \rangle_{\text{H}}^{1/2}$ is 0.1 Å for a pure bending motion of Mu(H) with respect to the bulk of the radical, using a bond length $l = 1.08$ Å and a force constant $k_\delta \cdot l^2 = 50 \text{ N m}^{-1}$. Thus, the difference in the effective radii is considerable ($\approx 9\%$ of the bond length) and makes an effect on the potential barrier plausible. The isotope effect $A_\mu \cdot \mu_p / A_p \cdot \mu_\mu$ for this radical at 190 K is 1.647, whereas the corresponding ratio for the Deuterium analogue at 188 K $A_d \cdot \mu_p / A_p \cdot \mu_d$ is 0.922 [91], in agreement with a preferred conformation $\theta_0=90^\circ$ for D. Related isotope effects for partly deuterated alkyl radicals have been explained in the same way [89].

The radical formed by Mu addition to tetramethylethylene exhibits a positive temperature dependence as does its H analogue [72, 92]. Thus, in terms of anisotropic rotational averaging the equilibrium conformation is $\theta_0 = 90^\circ$. Both the small temperature coefficient and the fact that A_μ is larger than A_p are compatible with the view that Mu is almost as large as a methyl group, and that we have essentially free rotation, i.e. a very small barrier. This seems strange if one compares rotational barriers for related molecules (c.f. $\approx 20\text{kJ/mol}$ for hexamethylethylene and $\approx 16\text{kJ/mol}$ for 2,3-dimethylbutane [93]). An alternative explanation for the temperature dependences of β -hfccs in substituted alkyl radicals has been suggested by Lloyd and Wood [94]. It is based on their experience with β -halo-t-butyl radicals, which are apparently non-planar at the radical centre. The temperature dependence of A_μ in the dimethylisopropylcarbiny radical



should then be governed by librational motion and by inversion at the radical centre. It would be more complicated than obtained from the $\cos^2\theta$ dependence (eq.4.44). We would still predict $A_\mu \cdot \mu_p / \mu_\mu > A_p$ because the bulkier Mu tends to avoid the neighbourhood of the methyl group. Which of the two explanations is true can only be decided after quantitative theoretical analysis. It may be noted that the peculiar temperature dependence of ^{13}C hfcc supports a non-planar structure of the t-butyl radical in hydrocarbon solution [95].

For the two radicals discussed above substitution of Mu by H does not much change the reduced moment of inertia for internal rotation. This is not so for the radical derived from acetone, $(\text{CH}_3)_2\dot{\text{C}}\text{OMu}$. Here, rotational motion of the hydroxyl group corresponds essentially to motion of Mu around the C-O axis. Replacement of Mu by H strongly changes the moment of inertia. This is most likely the reason for the observed isotope effect. $|A_{\text{p}}^{\text{OH}}|$ for $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and for the related $\text{H}_2\dot{\text{C}}\text{OH}$ are both very small [79], so it is not unreasonable to assume similar barriers and equilibrium conformations. For $\text{H}_2\dot{\text{C}}\text{OH}$ the barrier is 17kJ/Mol and θ_0 is 90° [72, 96]. This means that there is no free internal rotation but rather librational oscillation of OH in these radicals.

For the methyl substituted alkyl radicals derived from isoprene A_{p} (the one that corresponds to A_{μ}) takes the value for free rotation. A_{μ} is once more considerably greater than A_{p} , which indicates an equilibrium conformation with $|\theta_0| < 45^\circ$.

Yim and Wood [97] conclude from INDO calculations that the cyclohexadienyl radical is probably non-planar and inverts rapidly (Fig.4.12). For the muonium substituted analogue the potential for this inversion is asymmetric with respect to the ring plane, again because Mu appears bulkier than H and tends to avoid the ring plane with its interacting hydrogen atoms. Thus Mu resides preferentially in the endo position with its higher coupling constant. The same argument holds for H in the cyclohexadienyl- d_6 radical and for Mu in the cyclohexadienyl- d_6 , the methylcyclohexadienyl and the thiophenyl radicals. The asymmetry of such a potential has been determined to be ~ 600 J/mol from NMR-studies of cycloheptatriene with one deuterium substituted in the methylene group [98].

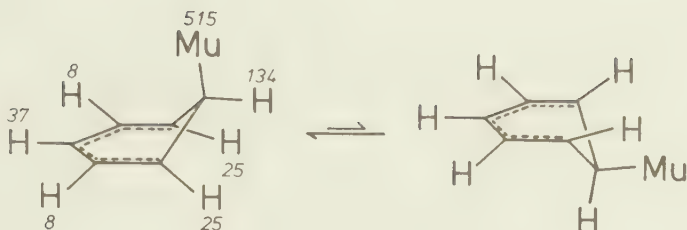


Fig.4.12: Conformational dynamics of the muonic cyclohexadienyl radical. Numbers denote the hfcc's (in MHz) for the muon, and for the protons in the hydrogen analogue.

The splitting of 1.5 MHz in each of the two radical frequencies in benzene at 1 kG (fig.4.8) identifies the observed species as the cyclohexadienyl radical. The doublet pattern and the size of the splitting are predicted correctly from perturbation theory (section 4.1.6) and are due to the methylene proton with its hfcc of 134 MHz. All other protons cause only a line broadening of ≈ 0.3 MHz at this field.

5. SUMMARY

This thesis is concerned with the chemistry of the light hydrogen isotope muonium in liquids, observed by muon spin rotation.

Rate constants for bimolecular reactions of muonium with various substrates in aqueous solution are determined directly for the first time. They disagree with earlier values obtained by indirect methods. The disagreement is mainly due to the model dependence of the earlier data. The rate constants are compared to those for the analogous reactions of H atoms. This reveals some large isotope effects, both positive and negative. Whereas Mu reacts faster than H with unsaturated or Br-substituted compounds the reverse is true for saturated alcohols. For the latter, model calculations based on activated complex theory are presented. They are in fair agreement with the experiments. They predict that for high reaction barriers the increase in tunneling probability for the reaction of the lighter isotope cannot compensate for the decrease in reaction rate which is caused by the increased barrier height due to zero point vibrational energy in the activated complex. For low barriers it may well be the reverse. Quantum mechanical calculations suggest that at room-temperature tunneling is an important pathway for chemical reactions of H isotopes, in particular for Mu.

It was found that the existing theory to describe muonium substituted free radicals was based on a wrong (truncated) hamiltonian. This was the reason for the failures in the efforts to observe these species. Theory, using the complete hamiltonian, is developed here and presented in full detail. It predicts that muonic radicals are to be observed most easily in high transverse magnetic

fields, i.e. in the Paschen-Back region, but that their detection in some special cases should be possible also in the absence of an external field. Both is confirmed experimentally. High field spectra yield the muon hyperfine coupling constant. In addition to this, the coupling constant of other magnetic nuclei and even their relative signs are extracted from zero field spectra. Large isotope effects are revealed when muon coupling constants and their temperature dependencies are compared to analogous proton data. They are interpreted in terms of incomplete rotational averaging of the coupling, based on isotope dependent barriers to internal rotation of the radicals.

It is confirmed that muonium behaves towards unsaturated compounds as a thermal hydrogen isotope.

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